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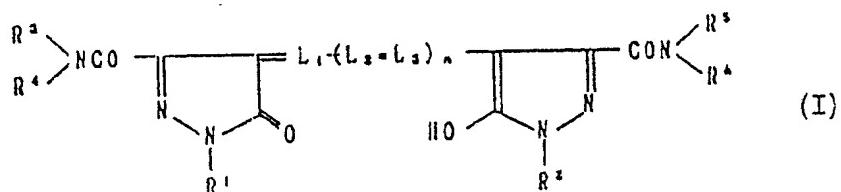
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(54) Silver halide photographic light-sensitive material containing oxonol dye.

(57) A silver halide photographic light sensitive material containing a water-soluble oxonol dye is disclosed. The dye is represented by the following Formula I:



wherein R¹ and R² are each a hydrogen atom, an alkyl group, an aryl group or an alkenyl group; R³, R⁴, R⁵ and R⁶ are each a hydrogen atom, an alkyl group, an aryl group, an alkenyl group or a heterocyclic group provided that at least one of said R³, R⁴, R⁵ and R⁶ is a heterocyclic group and R³ and R⁴, and R⁵ and R⁶ are respectively allowed to bond to form a heterocyclic ring; and the groups represented by said R¹ through R⁶ are allowed to be substituted or unsubstituted provided that at least one of said groups is a water-solubilizing group or a group having a water solubilizing group; L₁, L₂ and L₃ are each a substituted or unsubstituted methine group; and n is an integer of zero, 1 or 2.

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SILVER HALIDE PHOTOGRAPHIC LIGHT-SENSITIVE MATERIAL CONTAINING OXONOL DYE

FIELD OF THE INVENTION

This invention relates to a silver halide photographic light-sensitive material containing a oxonol dye and, particularly, to a silver halide photographic light-sensitive material containing a hydrophilic colloidal layer which is colored with a dye useful for a light-absorbing dye.

BACKGROUND OF THE INVENTION

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It has been well-known that a dye is added into a silver halide photographic light-sensitive material for the purpose of absorbing the rays of light having a specific wavelength so as to work as a filter, prevent halation and irradiation, or control sensitivity. The hydrophilic colloidal layers of the light-sensitive materials 15 are colored with these dyes.

A filter layer has usually been provided onto a light-sensitive emulsion layer or between an emulsion layer and another emulsion layer so as to play a role of making the rays of light incident to an emulsion layer be those of light having a preferable spectral composition. Also, for the purpose of improving the sharpness of photographic images, such a method has been taken in many cases as that an antihalation 20 layer is interposed between an emulsion layer and a support or is provided to the back of the support so that a halation may be prevented by absorbing harmful reflected light which was produced on the interface between the emulsion and the support or on the back of the support; or that harmful reflected or scattered light which was produced by silver halide grains or the like is absorbed by colored emulsion layer so that irradiation may be prevented.

25 The dyes which may be used with the above-mentioned purposes shall satisfy the following requirements; they shall have the characteristics of absorption spectra which excellently meet the purposes of use; they can completely be decolored in the course of photographic processing steps and/or can easily be eluted from a silver halide photographic light-sensitive material so that no residual color stain can be produced with the dyes after completing a development process; a photographic emulsion cannot be 30 affected by fog, desensitization, or the like; and the stability on standing can be excellent and neither discoloration nor color-fading can be produced in solutions or in the silver halide photographic light-sensitive material.

Heretofore, many efforts have been made and a number of dyes have been proposed with the purpose 35 of discovering the dyes capable of satisfying the above-mentioned requirements. For example, the oxonol dyes described in U.S. Patent No. 3,247,127, Japanese Patent Examined Publication Nos. 39-22069(1964) and 55-10059(1980), and so forth, have been well-known.

However, the present fact is that there has not yet been any dye having excellent characteristics capable of fully satisfying the above-mentioned requirements and of being applied to photographic light-sensitive materials.

40 In particular, a type of oxonol dyes having a carbamoyl group at the 3rd position have been described in British Patent No. 1,338,799, and Japanese Patent Publication Open to Public Inspection (hereinafter referred to as Japanese Patent O.P.I. Publication) Nos. 51-77327(1976), 58-143342(1983), 59-111641(1984), and 63-139944(1988), and so forth. Among them, the dyes described in British Patent No. 1,338,799 and Japanese Patent O.P.I. Publication No. 51-77327(1976) have not any solubilizing group in the molecular structures thereof and, therefore, insoluble to water or hardly soluble thereto.

45 In addition, the photographic processing has usually been carried out within a short time and under the low alkaline conditions. It is therefore, difficult to make these dyes elute completely from photographic material. It is also considered that the dyes having once been decolored may recur, or that the decolored dyes may exert a bad influence photographically even if they do not recur. Therefore, particularly in the case of using such a dye in a multi-layered photographic material for the above-mentioned purpose, it is 50 desired to make the dye water-soluble by introducing a water-solubilizing group into the dye. Resultingly, such a water-soluble dye may readily be eluted from the light-sensitive material in the course of the developing process. Therefore, the dye does not remain as it is.

In addition, if the dye is water-soluble, there is such an advantage that the dye may be added in the form of a aqueous solution into a photographic material. On the other hand, if the dye is hardly soluble to

water, an organic solvent or the like should be additionally used in combination. It is undesirable to do so from the viewpoint of harmfulness thereof.

The dyes described in Japanese Patent O.P.I. Publication Nos. 58-143342(1983), 59-111641(1984) and 63-139944(1988), each of which is an oxonol dye having a water-solubilizing group and a carbamoyl group at the 3rd position thereof, are not satisfactory in their characteristics, particularly in decoloring property. Therefore, these dyes have been required to be further improved from the above-mentioned viewpoint.

SUMMARY OF THE INVENTION

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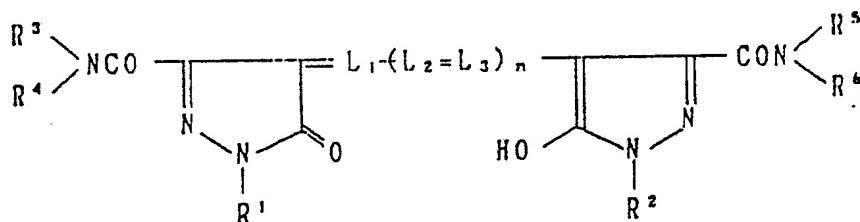
It is an object of the invention to provide a silver halide photographic light-sensitive material containing a water-soluble dye which is excellent in spectral absorption characteristics and photographically inert in the light-sensitive material and is readily decolored and/or eluted in the course of a photographic development process so as to produce very few stains after completing the photographic development process.

The above-mentioned object of the invention can be achieved with a silver halide photographic light-sensitive material containing a water-soluble oxonol dye represented by the following Formula I:

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Formula I

25



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wherein R¹ and R² are each a hydrogen atom, an alkyl group, an aryl group or a alkenyl group; R³, R⁴, R⁵ and R⁶ are each a hydrogen atom, an alkyl group, an aryl group, an alkenyl group or a heterocyclic group provided that at least one of the R³, R⁴, R⁵ and R⁶ is a heterocyclic group and R³ and R⁴, and R⁵ and R⁶ are respectively allowed to bond to form a heterocyclic ring; and the groups represented by the R¹ through R⁶ are allowed to substituted or unsubstituted provided that at least one of the groups is a water solubilizing group or a group having a water solubilizing group; L₁, L₂ and L₃ are each a substituted or unsubstituted methine group; and n is an integer of zero, 1 or 2.

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DETAILED DESCRIPTION OF THE INVENTION

The water-soluble oxonol dyes applicable to the invention are represented by Formula I. The groups represented by R¹ through R⁶ each denoted in the formula may further have a substituent or may not have any substituent. Such groups represented by R¹ through R⁶ will be exemplified below.

The alkyl groups represented by R¹ through R⁶ include, for example, a methyl group, an ethyl group, a propyl group, an isopropyl group, an n-butyl group, a tertiary butyl group, acyclopentyl group, and a cyclohexyl group. The alkyl groups include those each having a substituent. Such substituents include, for example, a hydroxy group, a cyano group, a sulfo group, a carboxyl group, halogen atoms such as a fluorine atom, a chlorine atom and a bromine atom, alkoxy groups such as a methoxy group and an ethoxy group, aryloxy groups such as a phenoxy group, a 4-sulfophenoxy group and a 2,4-disulfophenoxy group, aryl groups such as a phenyl group, a 4-sulfophenyl group and a 2,5-disulfophenyl group, alkoxy carbonyl groups such as a methoxycarbonyl group and an ethoxycarbonyl group, and aryloxycarbonyl groups such as a phenoxy carbonyl group.

The aryl groups represented by R¹ through R⁶ include those each having a substituent. The aryl groups include, for example, a phenyl group, a 2-methoxyphenyl group, a 4-nitrophenyl group, a 3-chlorophenyl group, a 4-aminophenyl group, a 4-hydroxyphenyl group, a 4-methanesulfonylphenyl group, a 4-sulfophenyl group, a 3-sulfophenyl group, a 2-sulfophenyl group, a 2-methyl-4-sulfophenyl group, a 2-chloro-4-sulf-

- fophenyl group, a 4-chloro-3-sulfophenyl group, a 2-chloro-5-sulfophenyl group, a 2-methoxy-5-sulfophenyl group, a 2-hydroxy-4-sulfophenyl group, a 2,5-dichloro-4-sulfophenyl group, a 2,6-diethyl-4-sulfophenyl group, a 2,5-disulfophenyl group, a 3,5-disulfophenyl group, a 2,4-disulfophenyl group, a 4-phenoxy-3-sulfophenyl group, a 2-chloro-6-methyl-4-sulfophenyl group, a 3-carboxy-2-hydroxy-5-sulfophenyl group, a 4-carboxyphenyl group, a 2,5-dicarboxyphenyl group, a 3,5-dicarboxyphenyl group, a 2,4-dicarboxyphenyl group, a 3,6-disulfo- α -naphthyl group, an 8-hydroxy-3,6-disulfo- α -naphthyl group, a 5-hydroxy-7-sulfo- β -naphthyl group, and a 6,8-disulfo- β -naphthyl group.

5 The alkenyl groups represented by R¹ through R⁶ include, for example, a vinyl group and an allyl group, and such alkenyl groups include those each having a substituent.

- 10 The heterocyclic groups represented by R³ through R⁶ include those each having a substituent. Such heterocyclic groups include, for example, pyridyl groups such as a 2-pyridyl group, a 3-pyridyl group, a 4-pyridyl group, a 5-sulfo-2-pyridyl group, a 5-carboxy-2-pyridyl group, a 3,5-dichloro-2-pyridyl group, a 4,6-dimethyl-2-pyridyl group, a 6-hydroxy-2-pyridyl group, a 2,3,5,6-tetrafluoro-4-pyridyl group and a 3-nitro-2-pyridyl group, oxazolyl groups such as a 5-sulfo-2-benzoxazolyl group, a 2-benzoxazolyl group and a 2-oxazolyl group, thiazolyl groups such as a 5-sulfo-2-benzthiazolyl group and a 2-thiazolyl group, imidazolyl groups such as a 1-methyl-2-imidazolyl group, a 1-methyl-5-sulfo-2-benzimidazolyl group, furyl groups such as a 3-furyl group, pyrrolyl groups such as a 3-pyrrolyl group, thienyl groups such as a 2-thienyl group, pyrazinyl groups such as a 2-pyrazinyl group, pyrimidinyl groups such as a 2-pyrimidinyl group and a 4-chloro-2-pyrimidinyl group, pyridazinyl groups such as a 2-pyridazinyl group, purinyl groups such as an 8-purinyl group, isoaxazolinyl groups such as a 3-isoaxazolinyl group, selenazolyl groups such as a 5-sulfo-2-selenazolyl group, sulforanyl groups such as a 3-sulforanyl group, piperidinyl groups such as a 1-methyl-3-piperidinyl group, pyrazolyl groups such as a 3-pyrazolyl group, and tetrazolyl groups such as a 1-methyl-5-tetrazolyl group.

20 In R³ through R⁶, R³ and R⁴, and R⁵ and R⁶ are capable of bonding to complet a ring. Such rings include, for example, a piperazyl group, a piperidyl group, a morpholino group and those each having a substituent.

- 25 At least one of the groups represented by R¹ through R⁶ is required to have a substituent solubilizing group such as a sulfo group, a sulfinyl group, a carboxyl group, a phosphono group, a phosphoryl group, a hydroxyl group, a sulfuric acid ester group, or a group containing one of the above-given groups so as to 30 serve as a group capable of giving water-solubility to the dye.

The oxonol dyes of the invention will be more preferable when R³ and R⁵ represent each a hydrogen atom or an alkyl group and R⁴ and R⁶ represent heterocyclic groups which may be the same with or the different from each other, and will be further preferable when R³ and R⁵ represent each a hydrogen atom, and R⁴ and R⁶ represent heterocyclic groups which may be the same with or the different from each other.

- 35 It will be particularly preferable when R³ and R⁵ each represent a hydrogen atom and R⁴ and R⁶ represent each the same heterocyclic group. In this case, it is necessary that the nitrogen atom of amido at the third position of the pyrazolone ring should bond to a carbon atom of a heterocyclic ring represented by R⁴ or R⁶.

Some typical examples of the dyes represented by Formula I, which may be applied to the invention, 40 will be given below. It is, however, to be understood that the invention shall not be limited to the dyes given below.

Exemplified Compound

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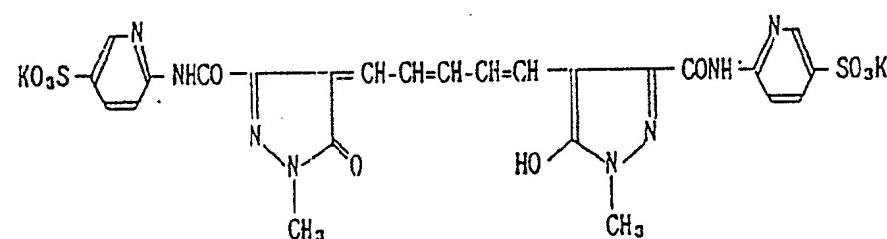
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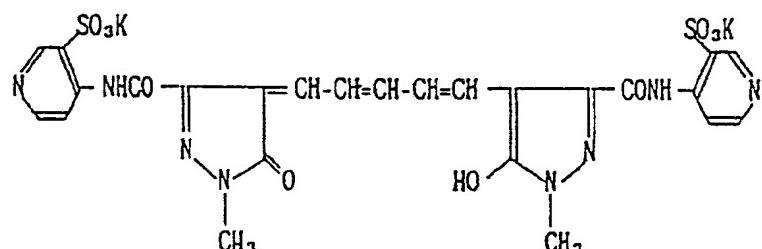
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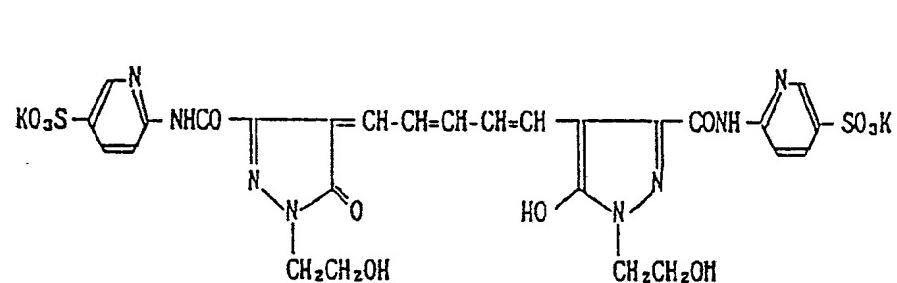
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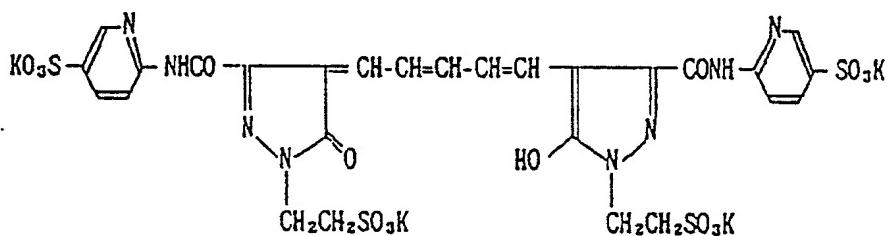


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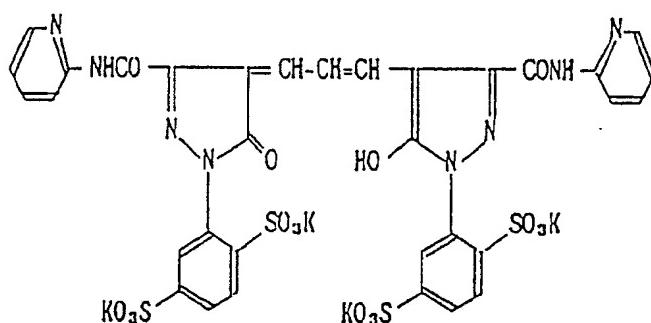
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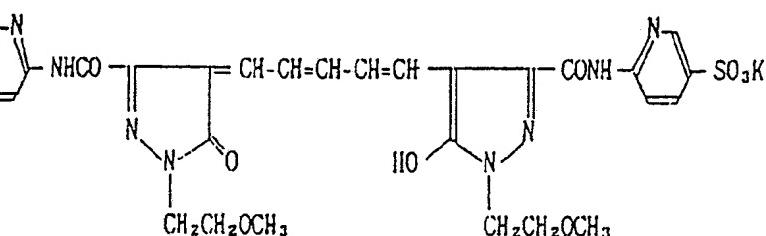
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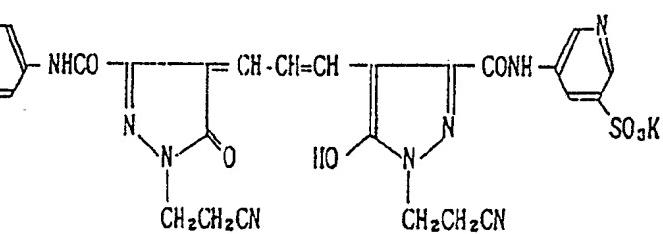
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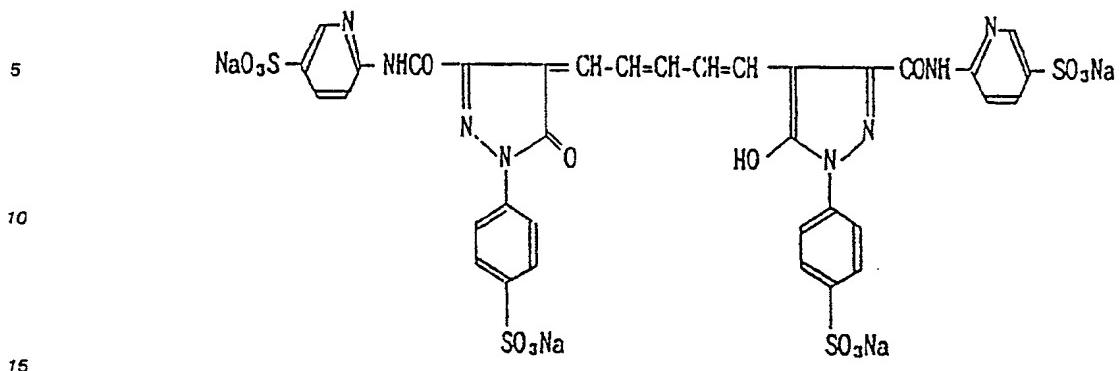
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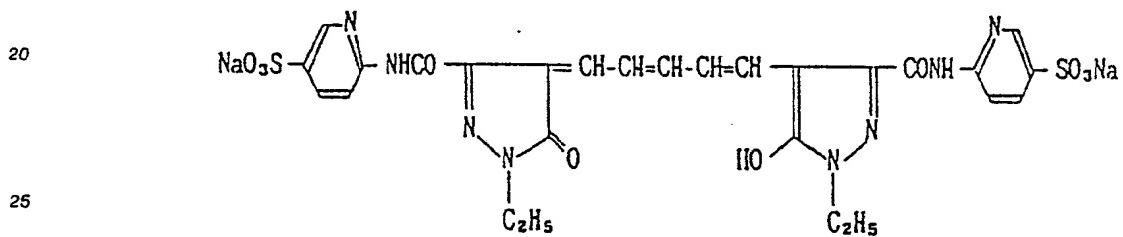
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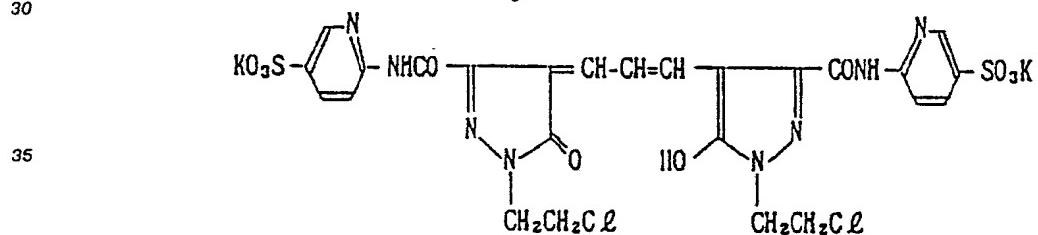
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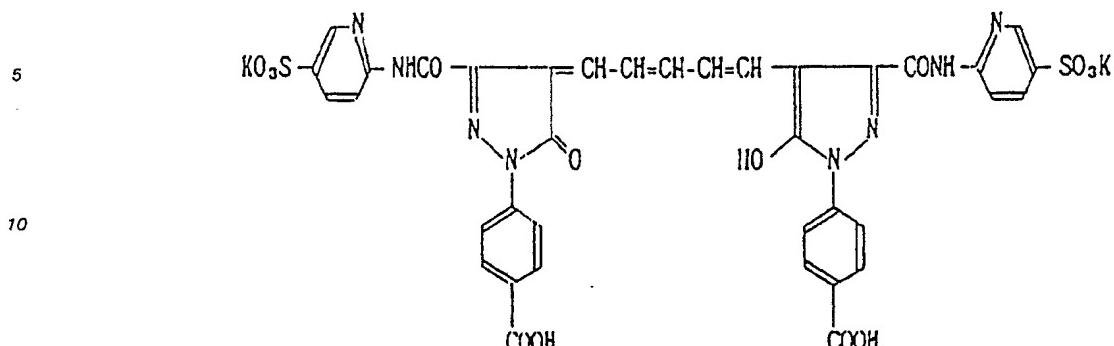
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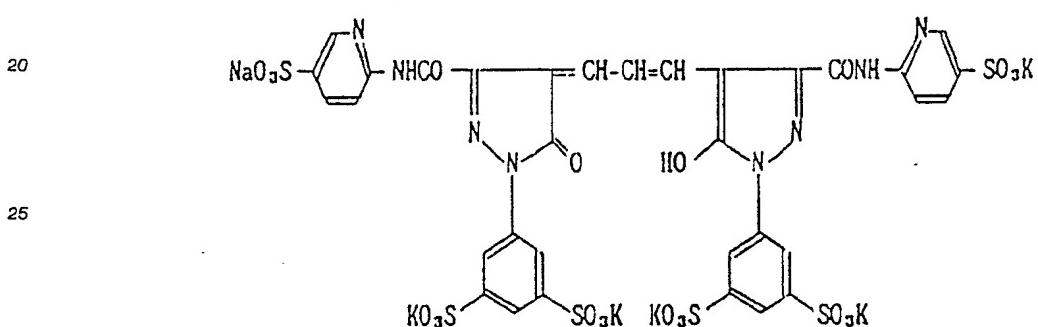
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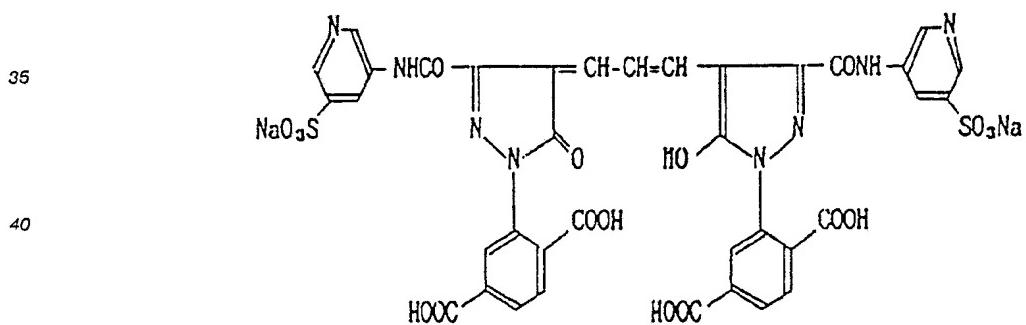
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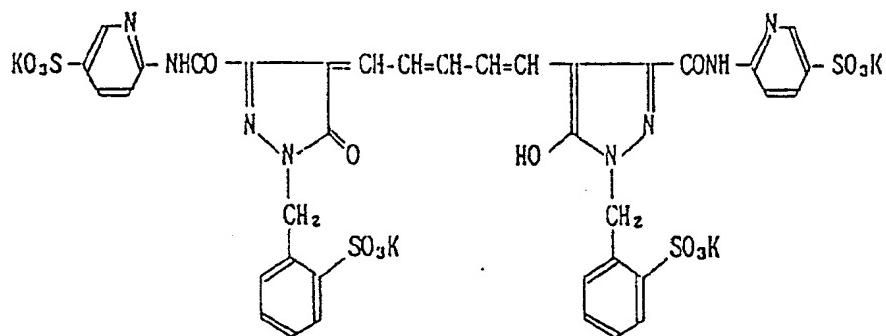
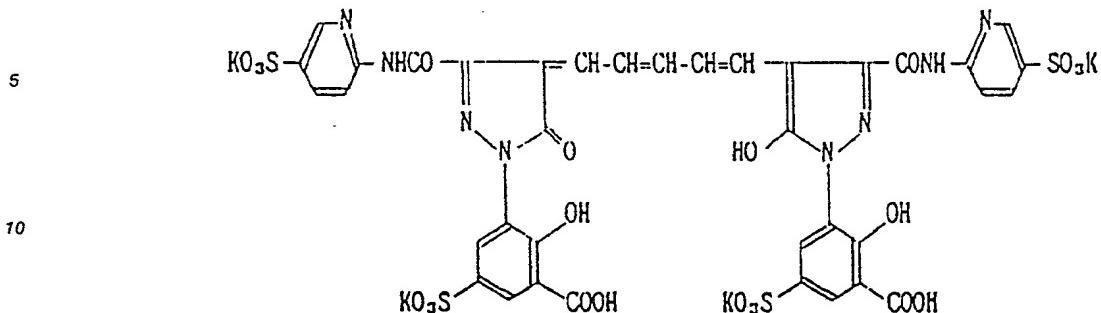
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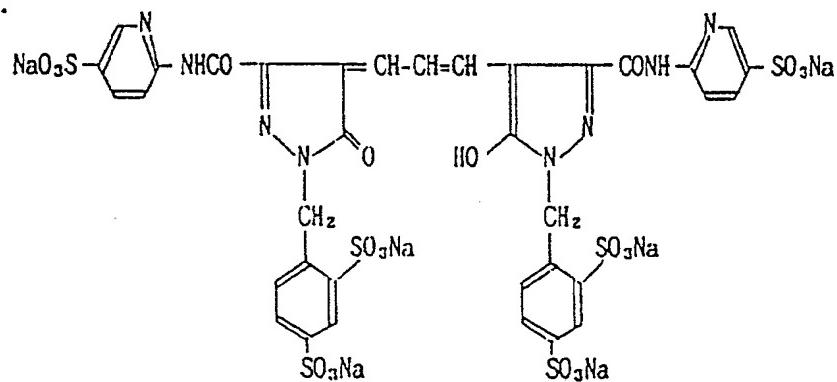
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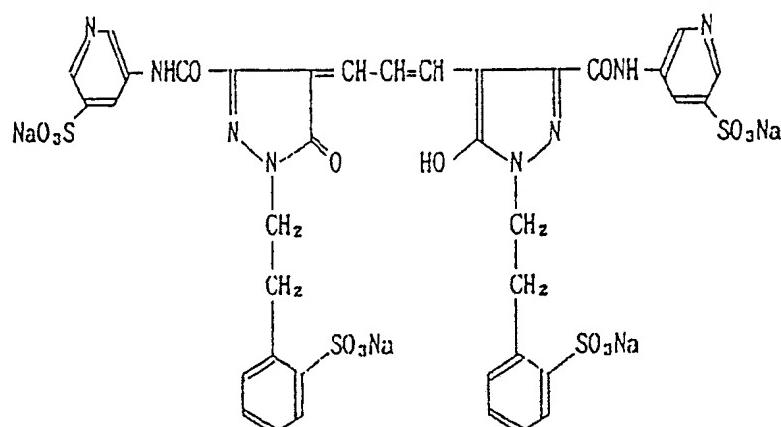


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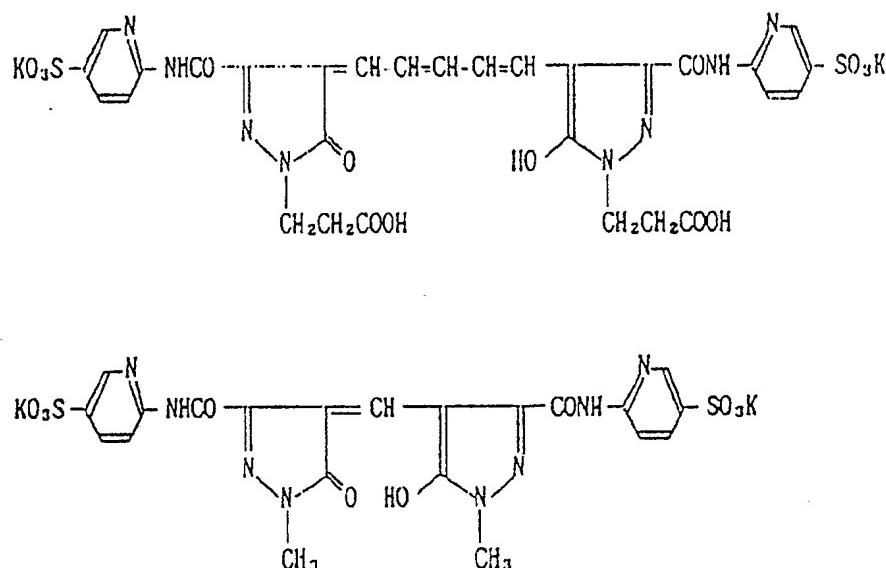
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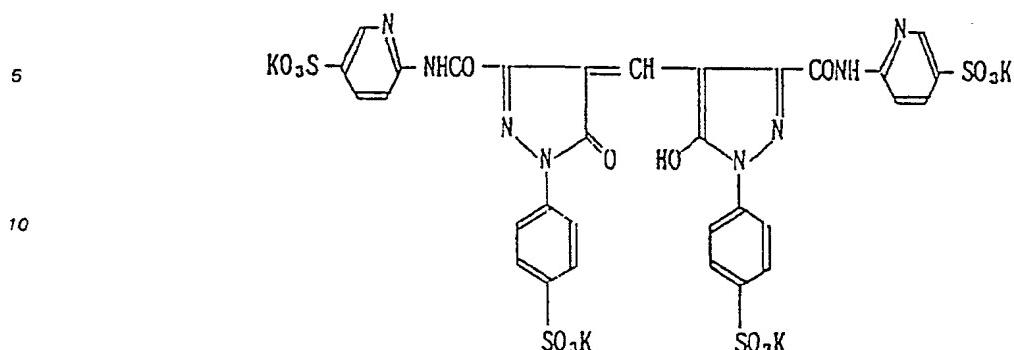
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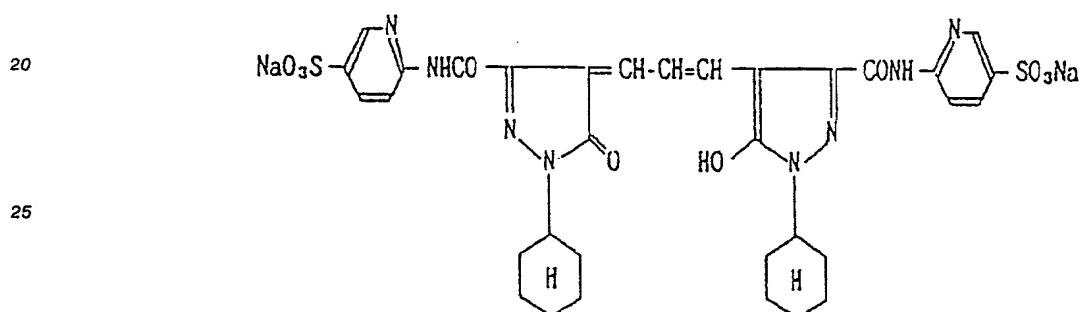


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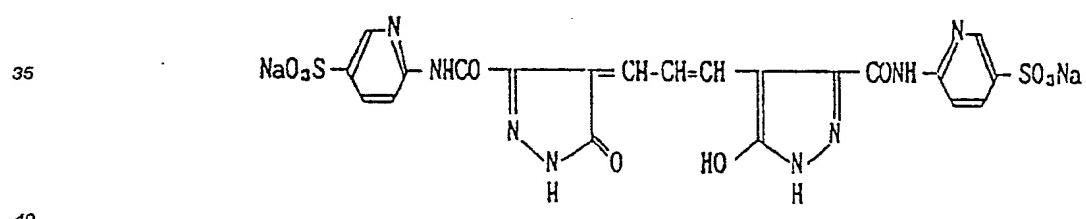
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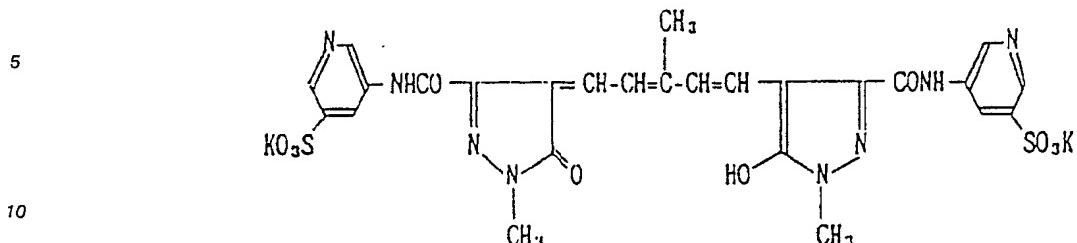
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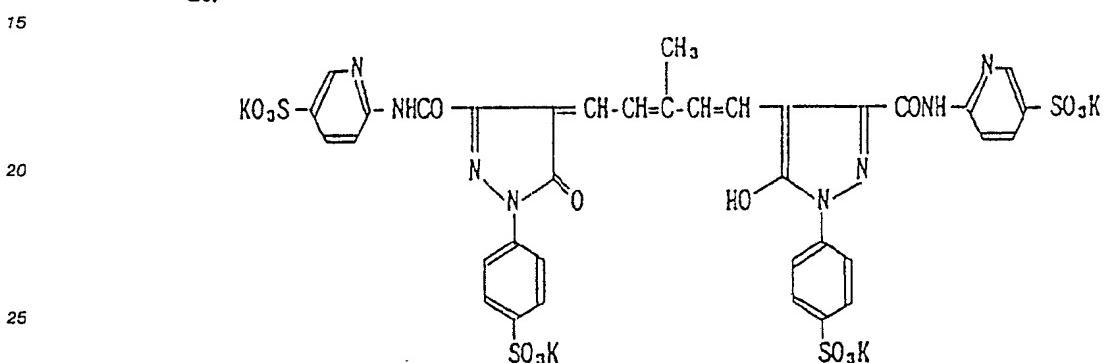
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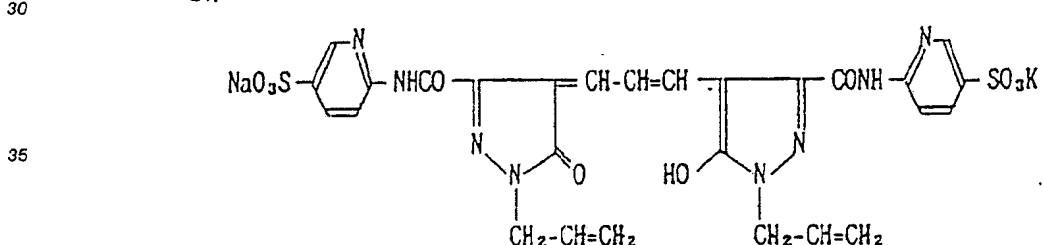
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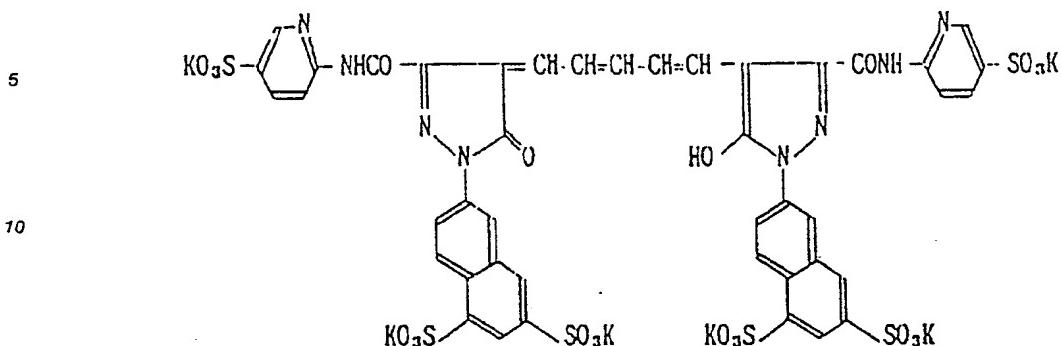
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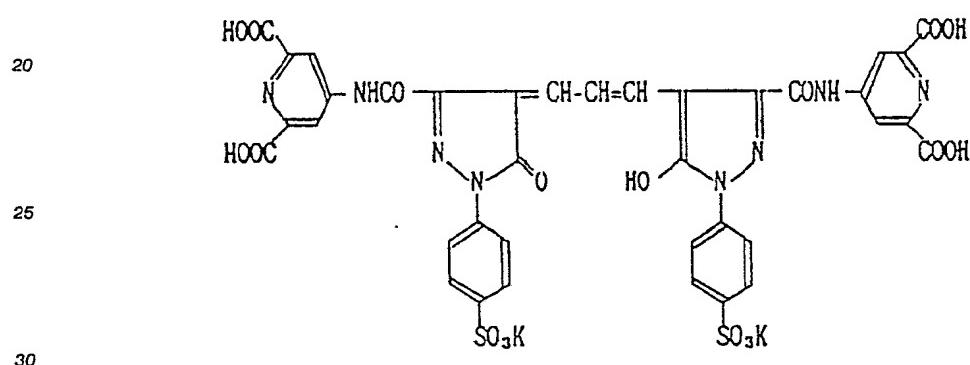
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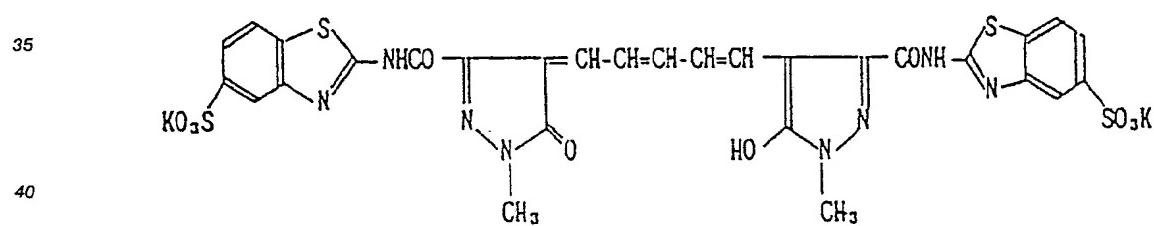
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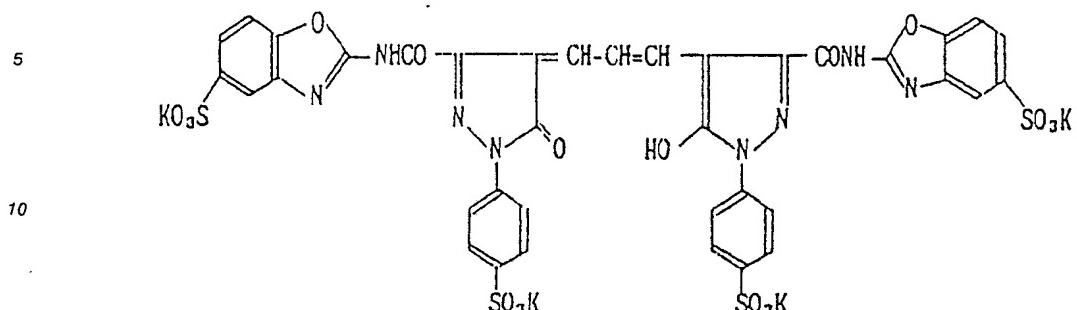


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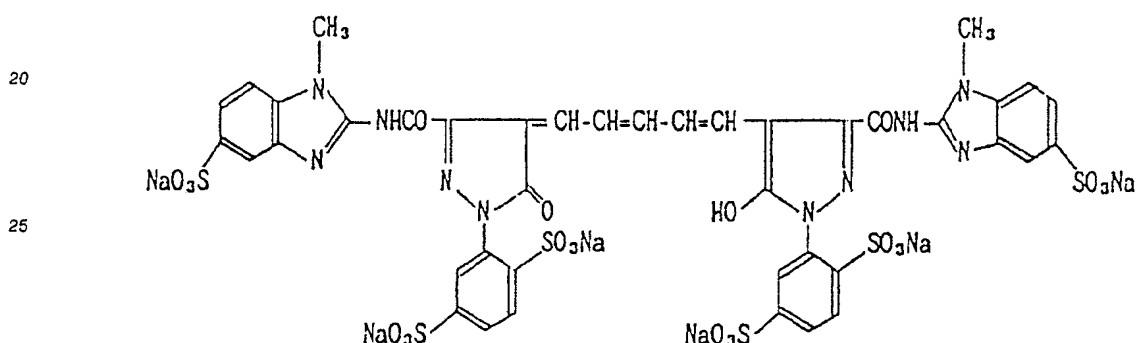
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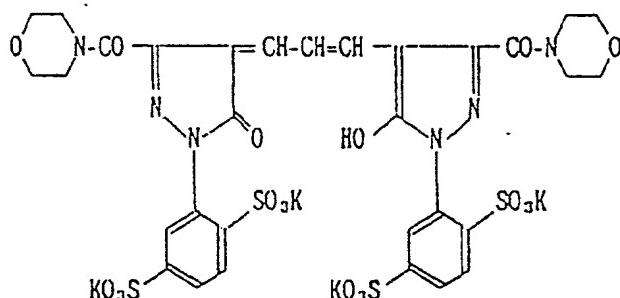
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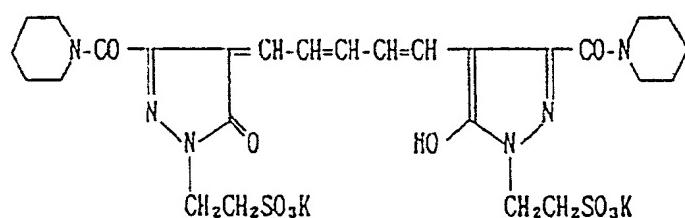
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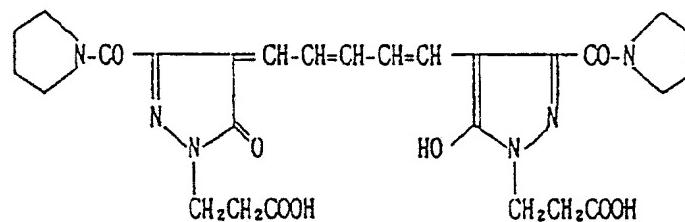
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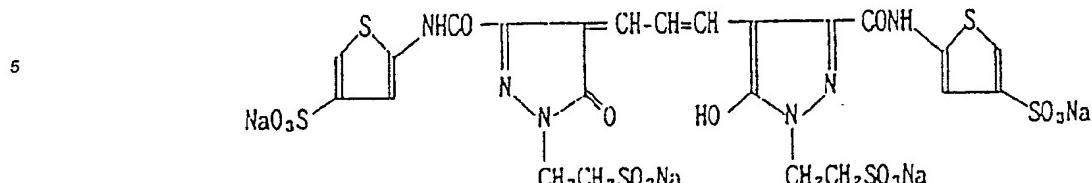
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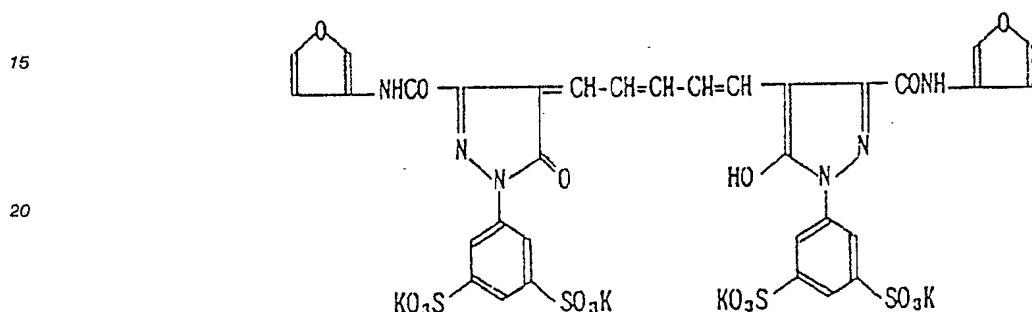
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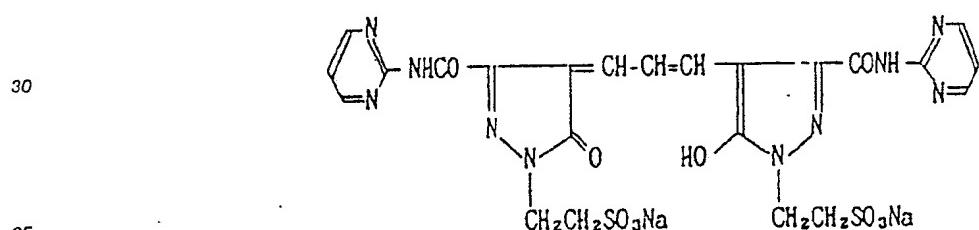
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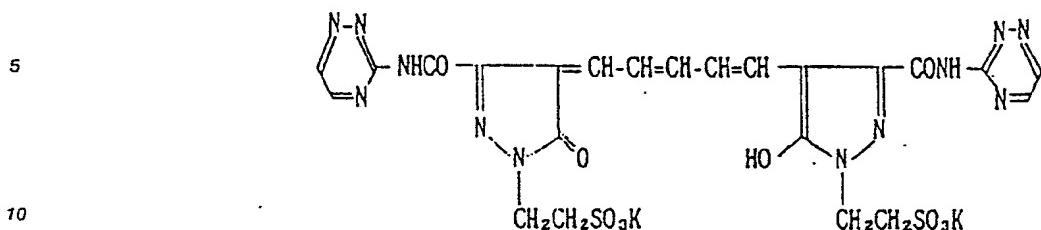
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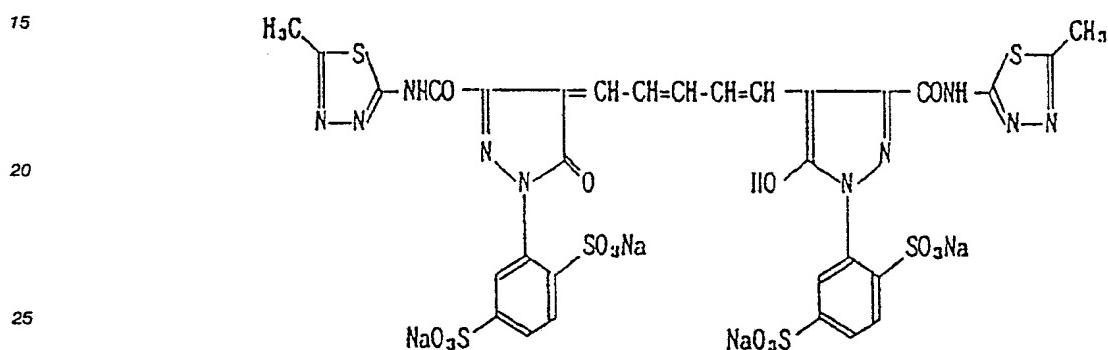
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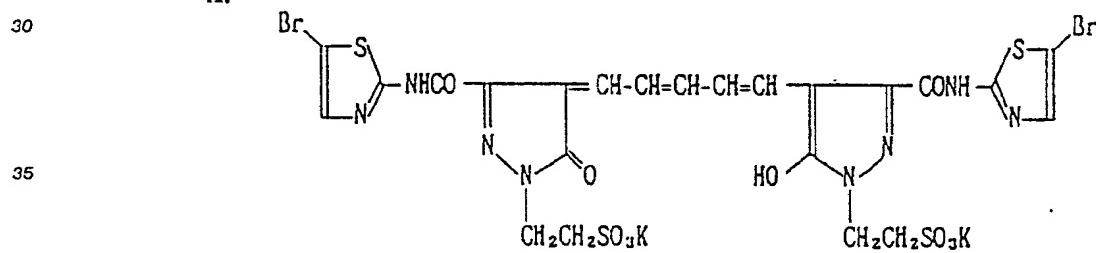
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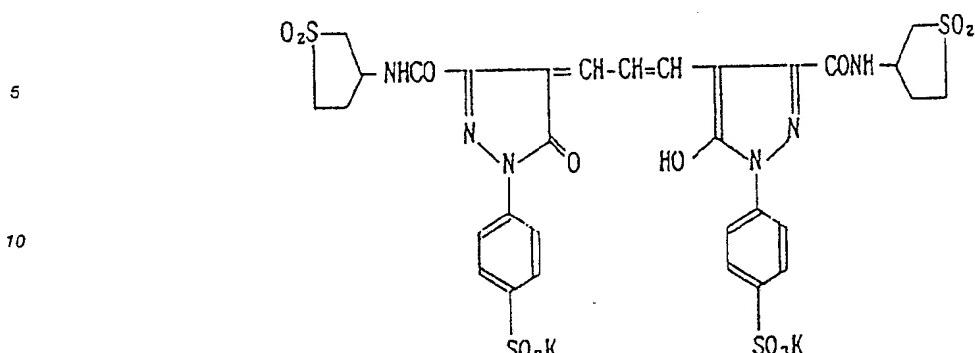
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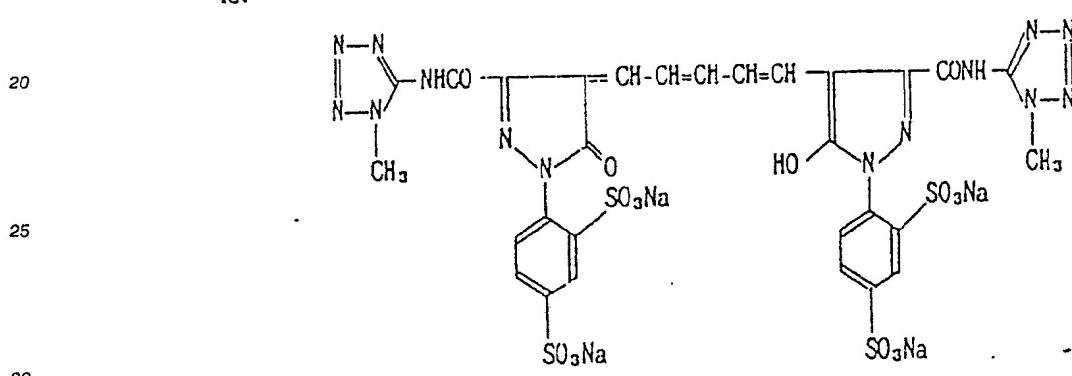
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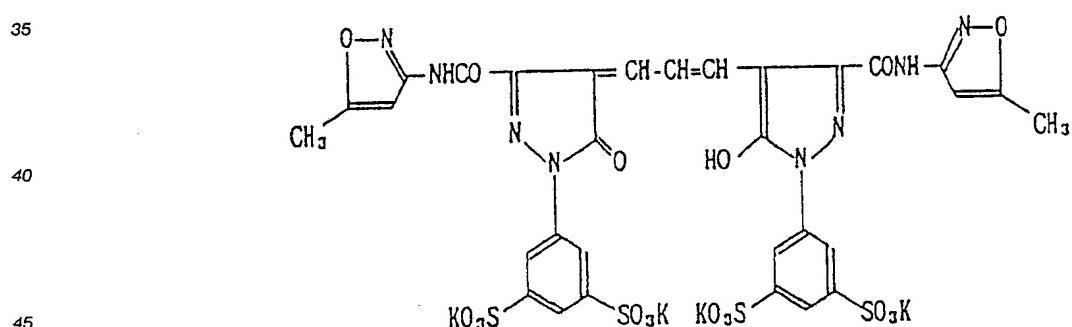
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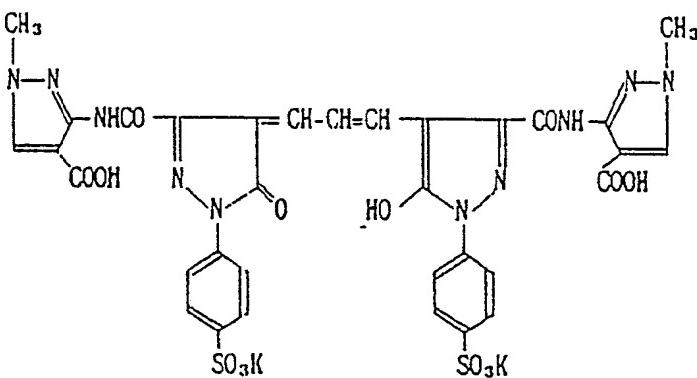
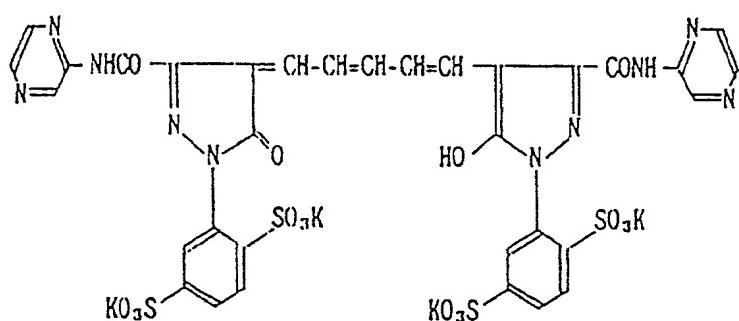
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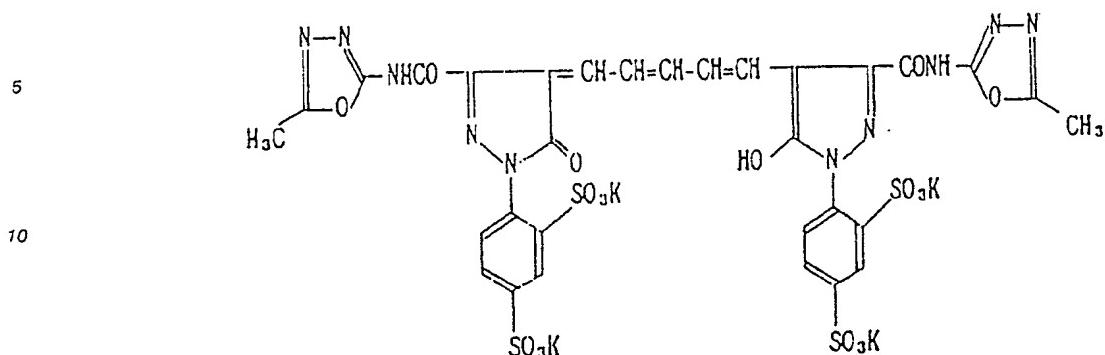
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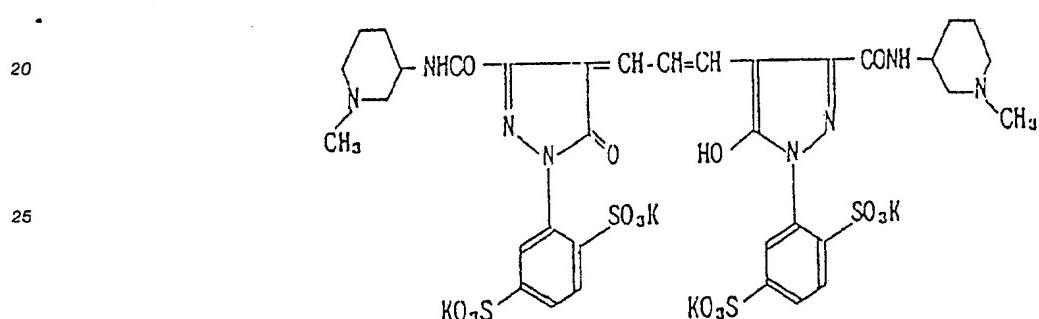
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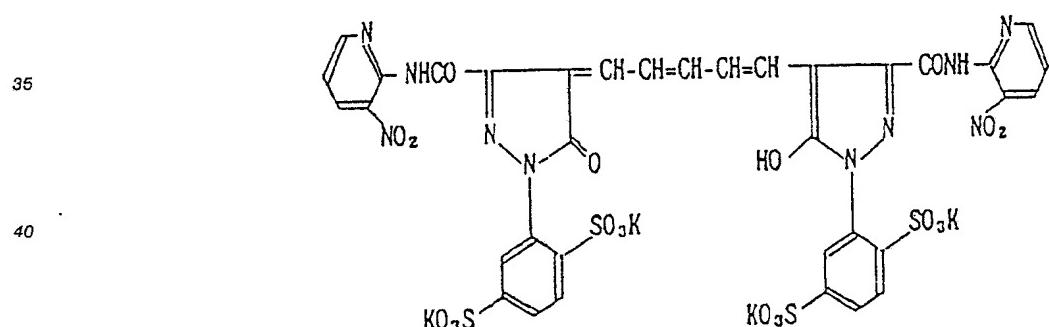
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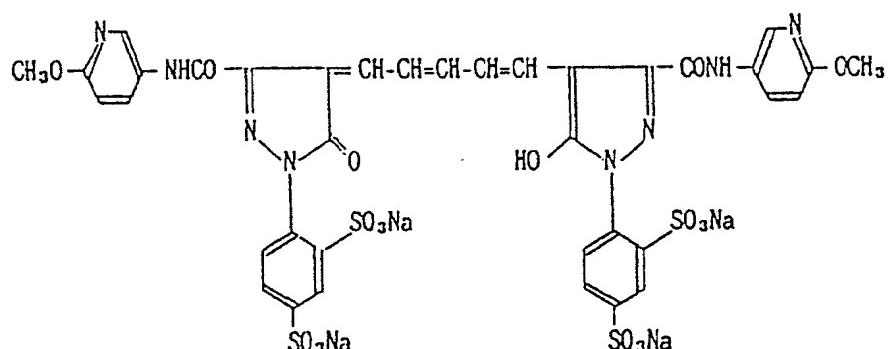
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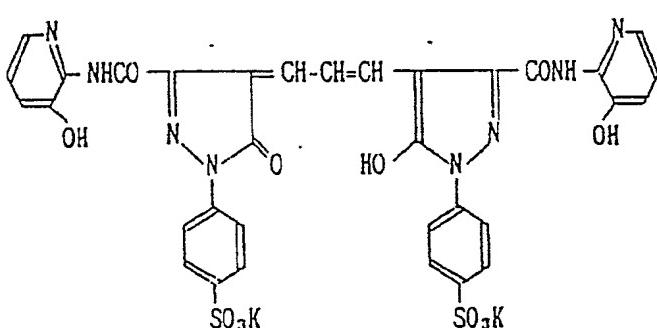
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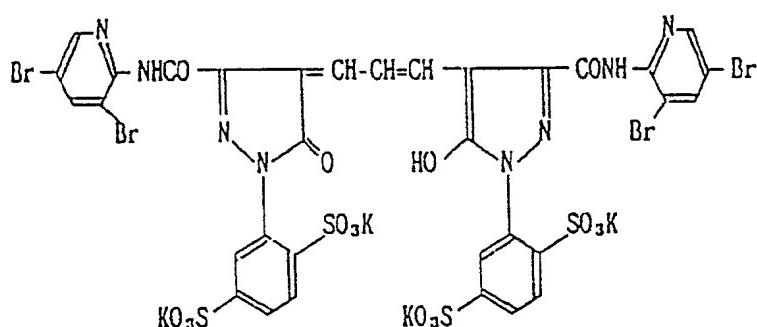
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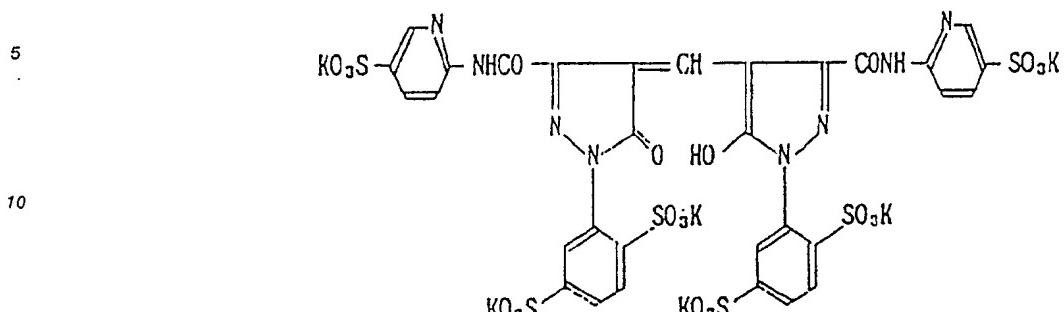


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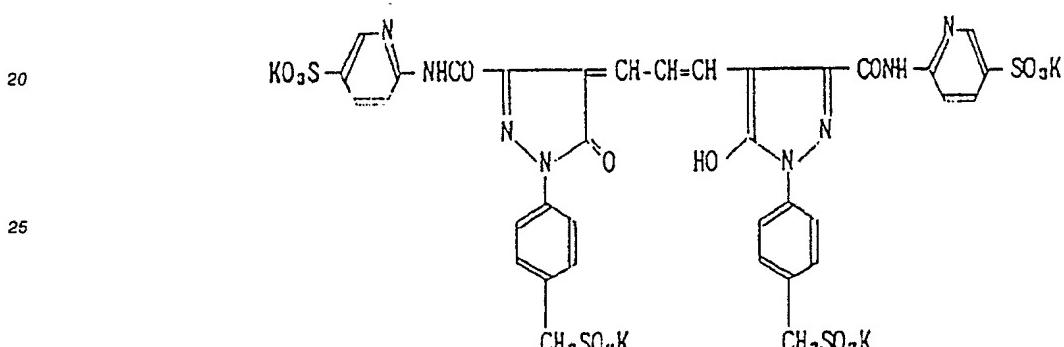
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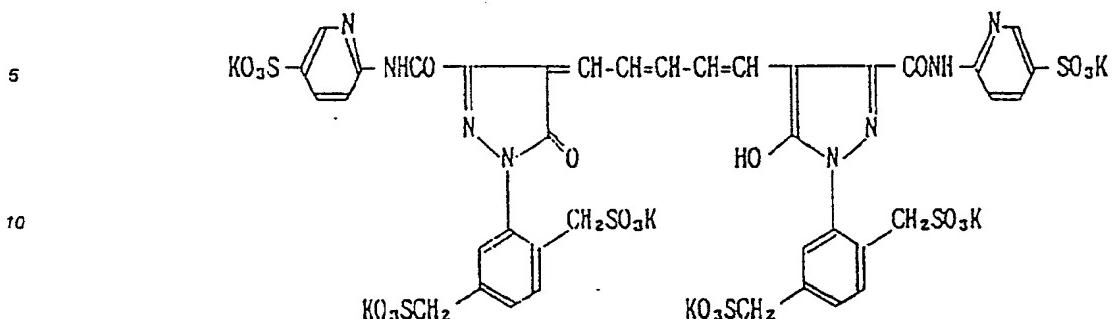
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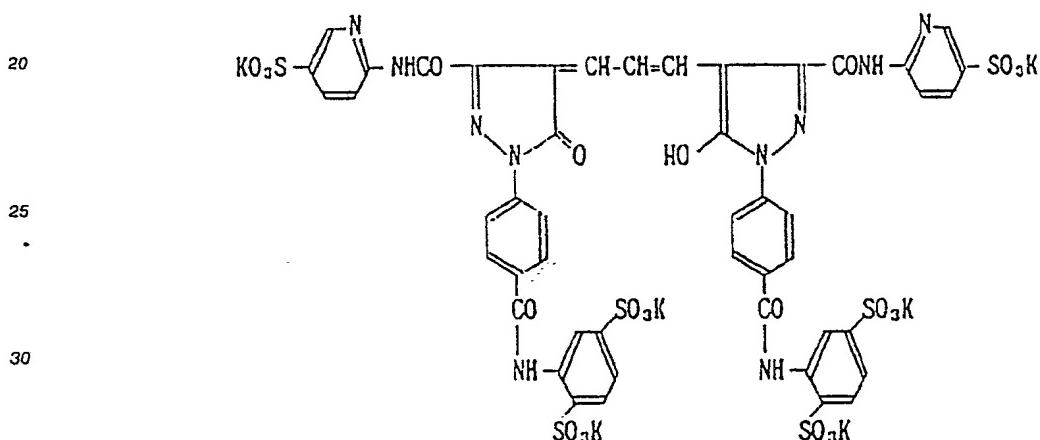
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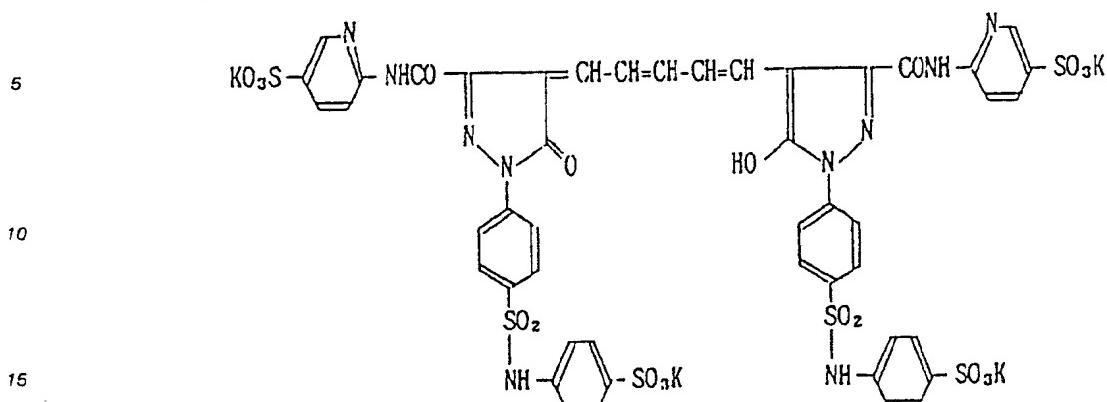
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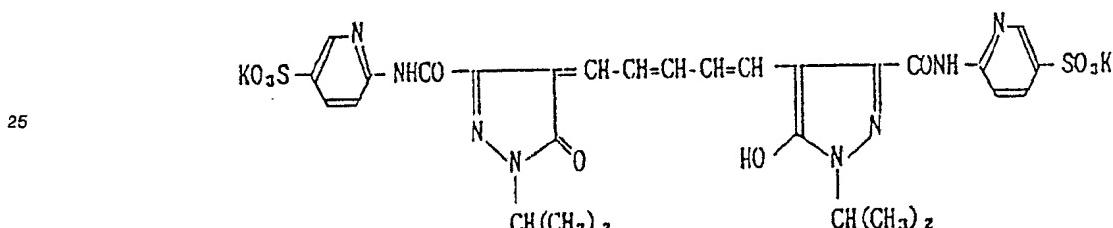
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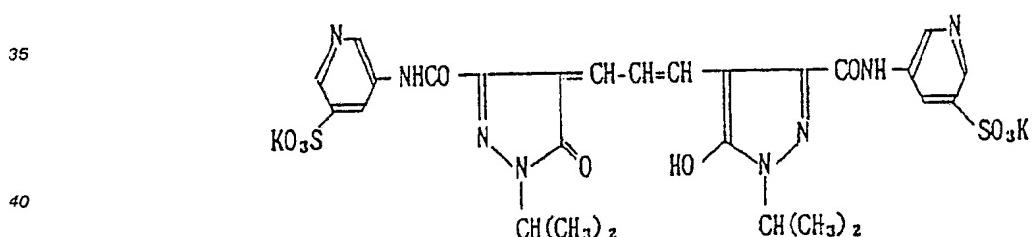
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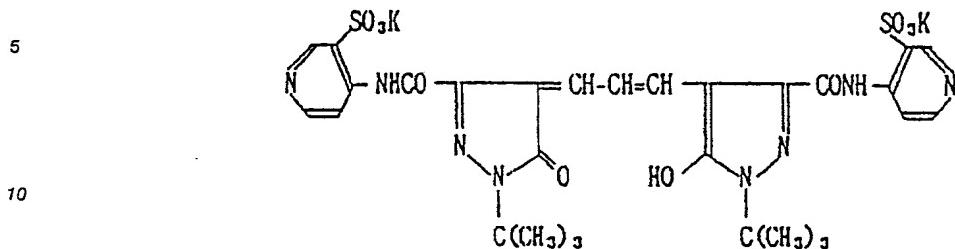


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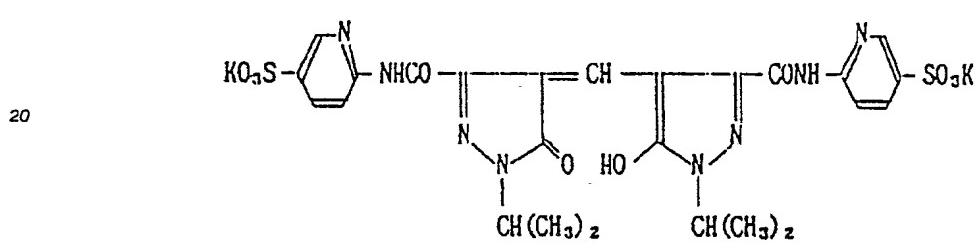
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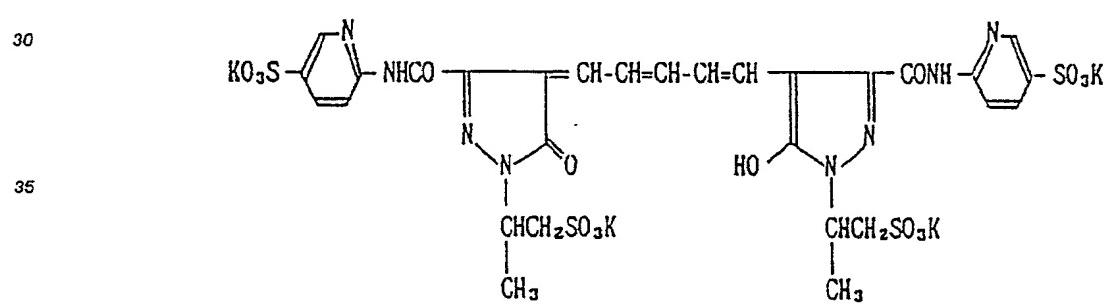
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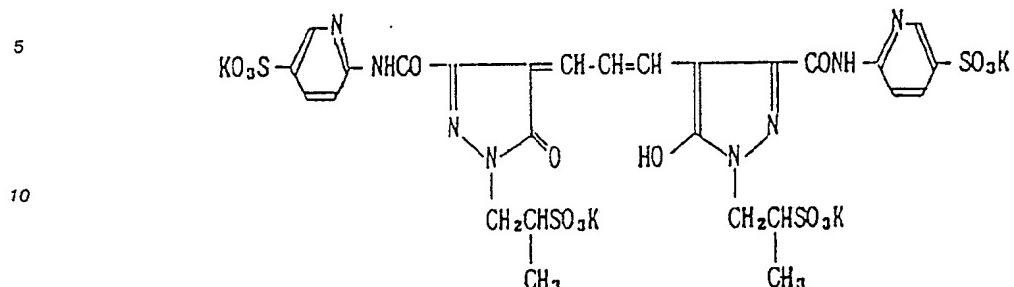


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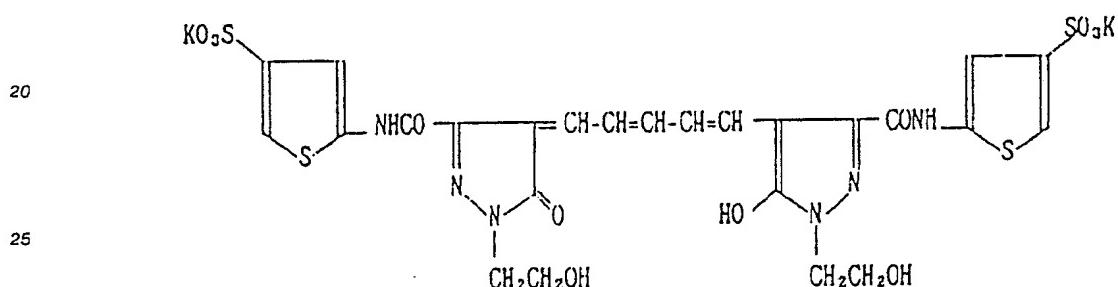
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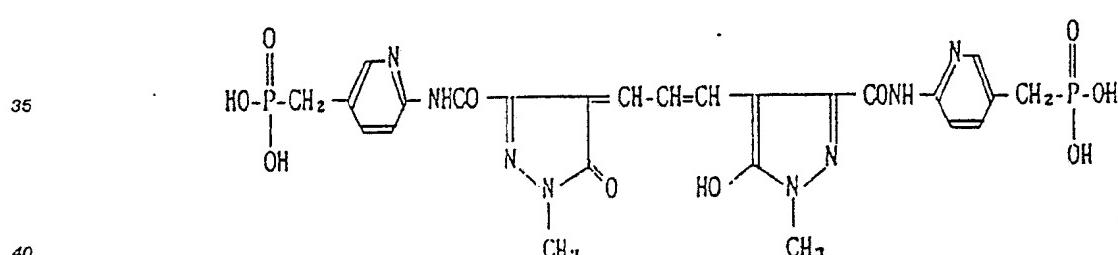
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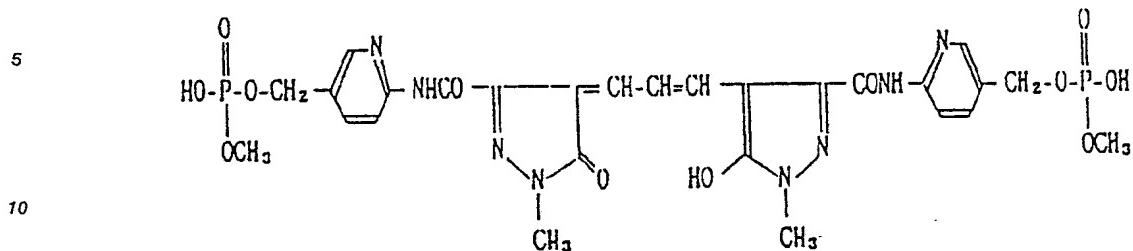


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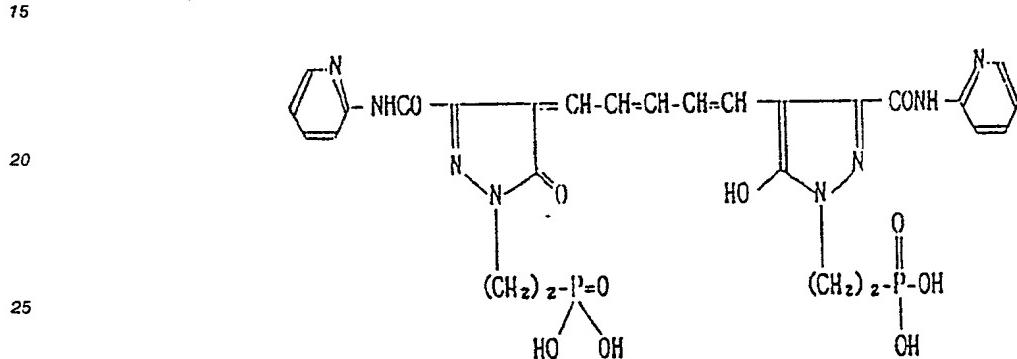
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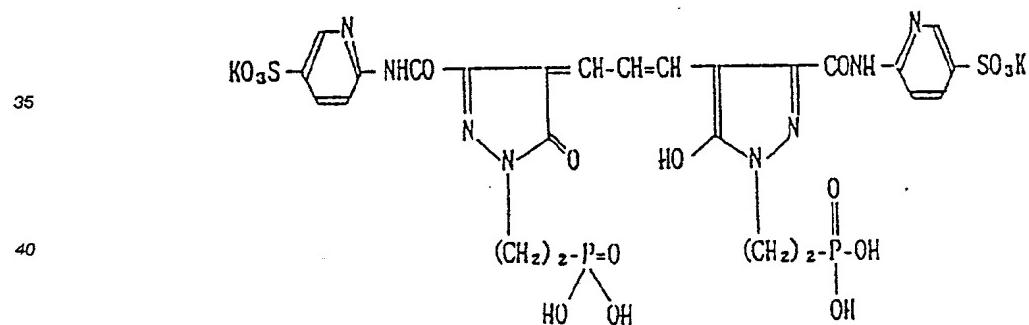
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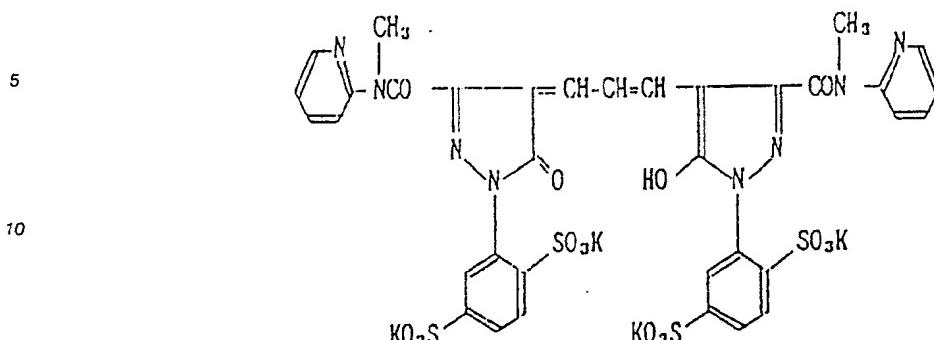


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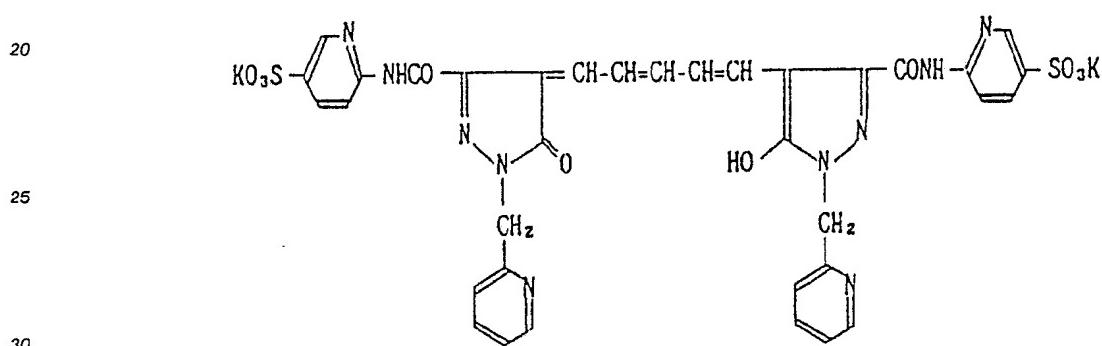
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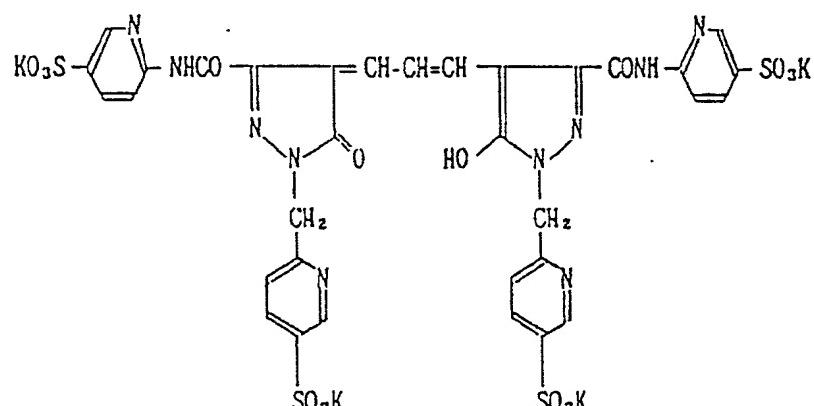
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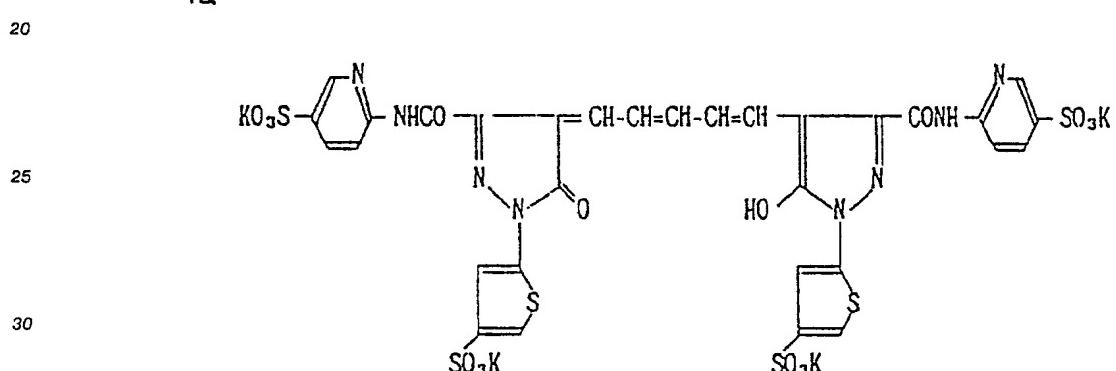
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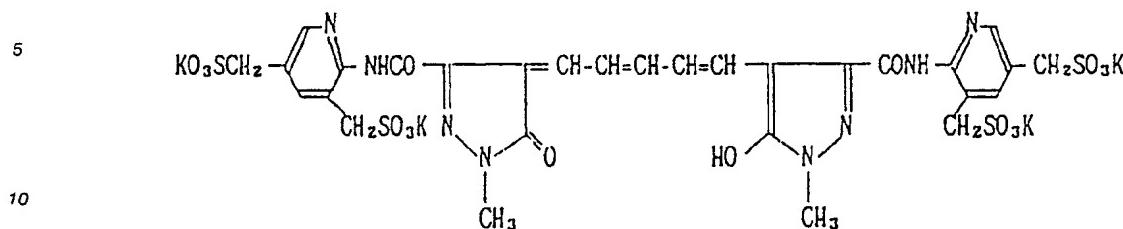
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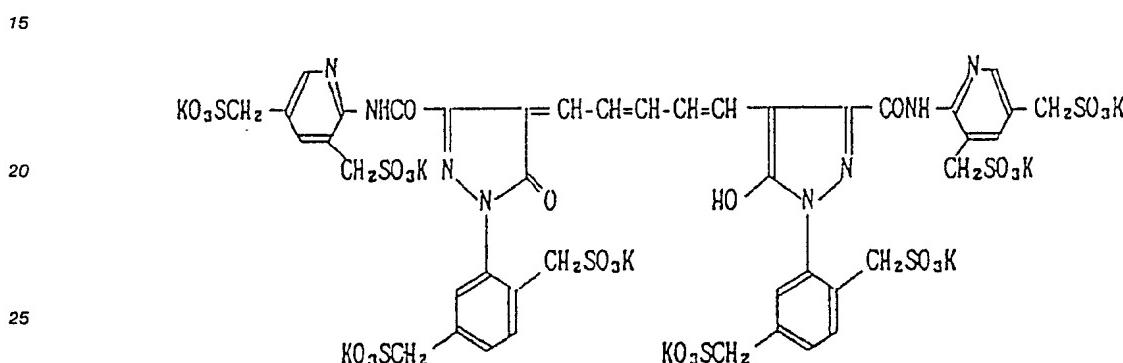
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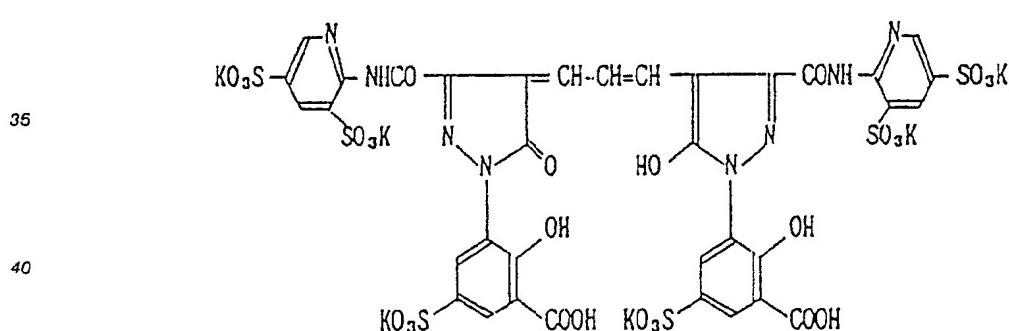
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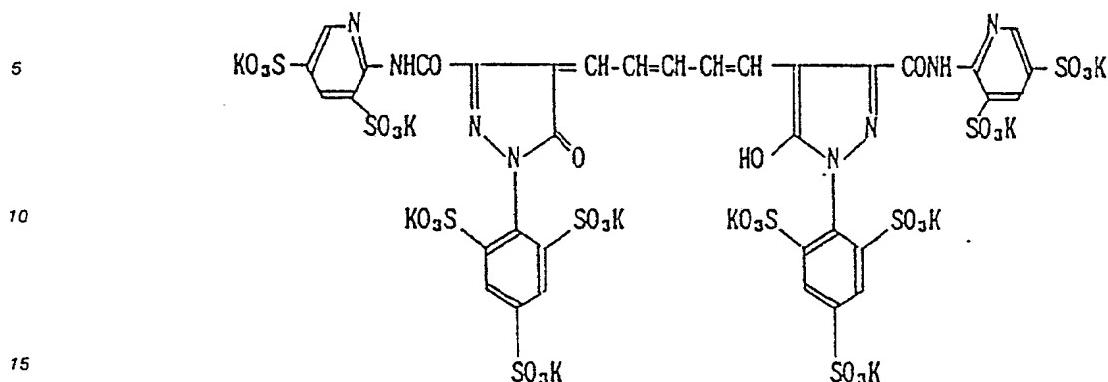


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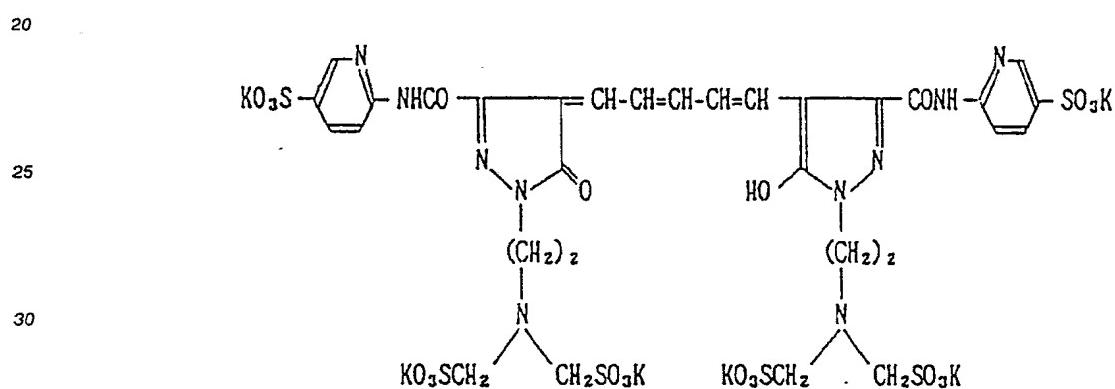
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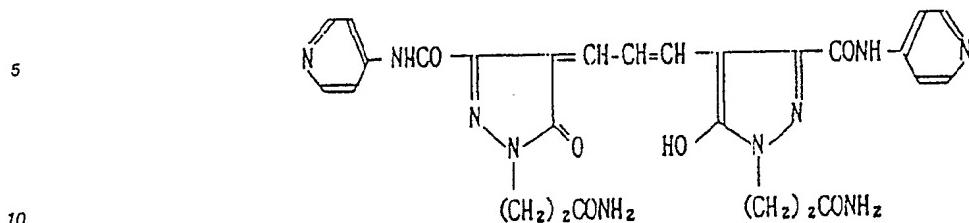
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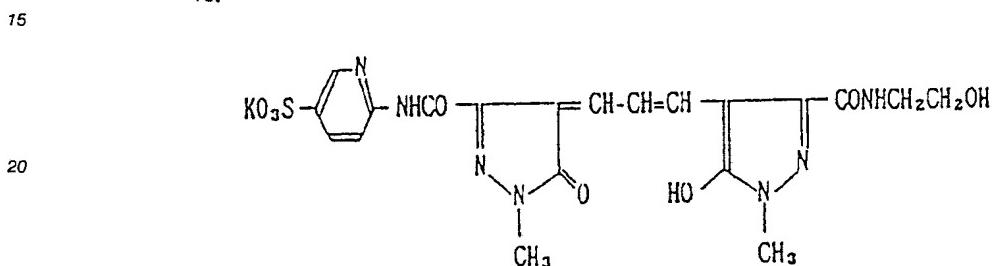
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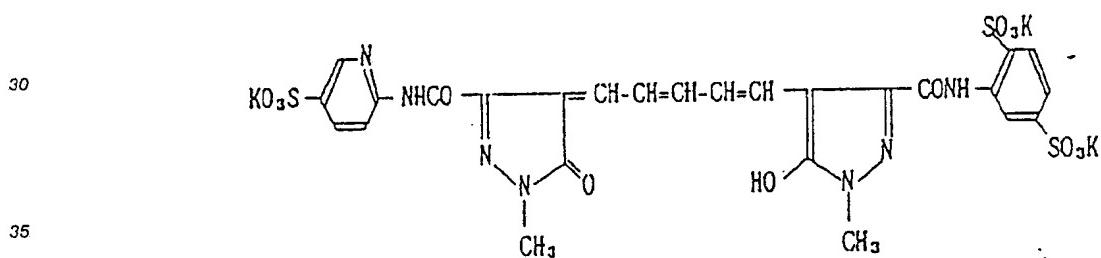
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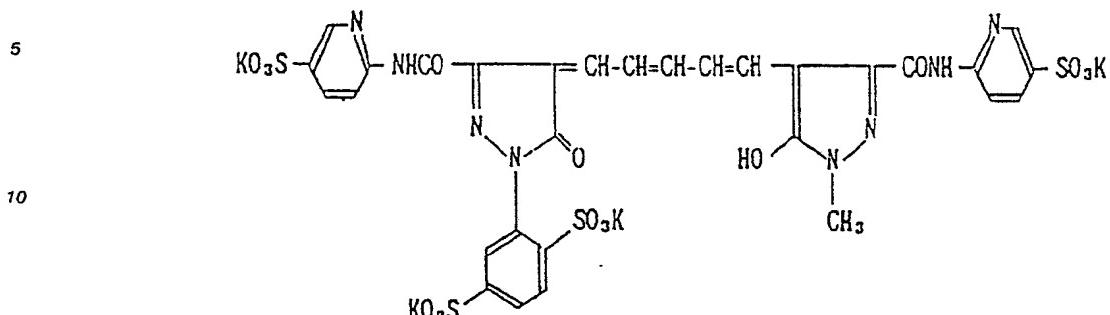
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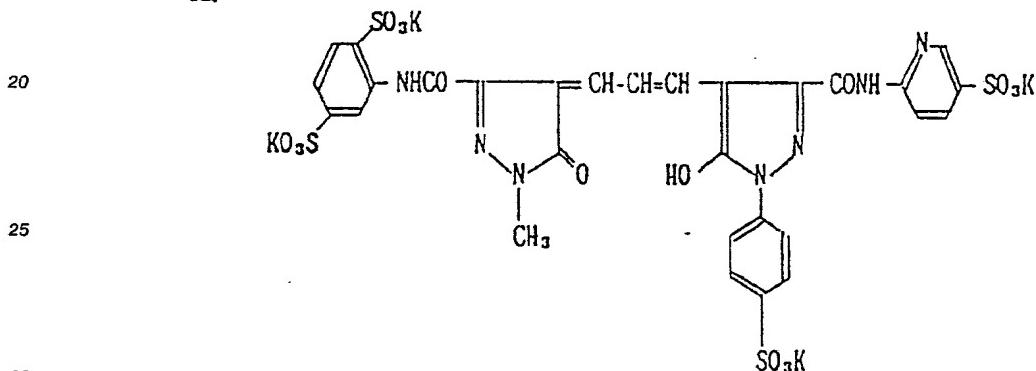
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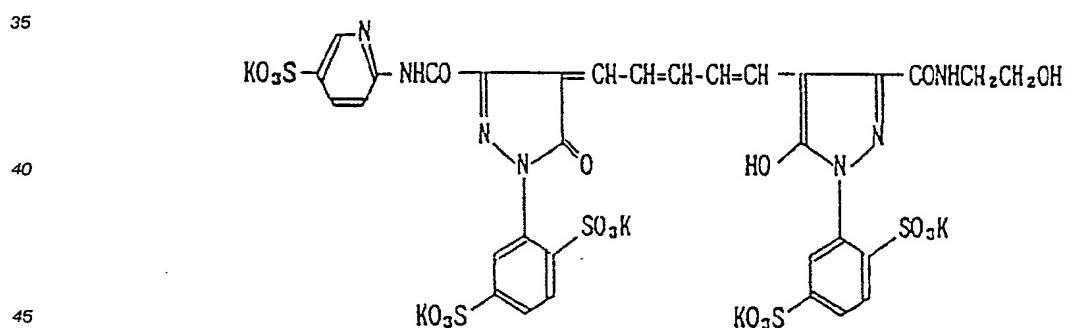
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The oxonol dyes applicable to the invention may readily be synthesized by the skilled in the art in the same manner as described in Japanese Patent O.P.I. Publication No. 58-143342(1983).

50 In the light-sensitive materials of the invention, the oxonol dyes represented by the foregoing formula may be added into silver halide photographic light-sensitive emulsions so as to serve as an antiirradiation dye, or they may also be added into non-light-sensitive hydrophilic colloidal layers so as to serve as a filter dye or an antihalation dye. It is also allowed to use them in combination or to use them together with the other dyes so as to meet the purposes of the use. The dyes relating to the invention may readily be added into the silver halide photographic light-sensitive emulsions or the other hydrophilic colloidal layers, in an ordinary method. The dyes are added into a photographic material usually in such a manner that the dye or the organic or inorganic alkali salt thereof is dissolved in water to make a suitably concentrated aqueous

dye solution and the resulting solution is added into a coating solution and, then, the coating is carried out in a well known method, so that the dye is added into the photographic material. The dye content of a light-sensitive material depends on the purpose of the use. However, the dye is usually coated in an amount within the range of 1 to 800 mg per sq. meter of the light-sensitive material.

- 5 The materials of the supports of the photographic materials of the invention include, for example, a cellulose acetate film, a cellulose nitrate film, a polyester film such as those of polyethyleneterephthalate, a polyolefin film such as those of polyethylene, a polystyrene film, a polyamide film, a polycarbonate film, a baryta paper, a polyolefin-coated paper, a polypropylene synthetic paper, a glass plate, and a metal plate. These supports may suitably be selected out to meet the purposes of using a photographic material.
- 10 The hydrophilic colloids applicable to the photographic materials of the invention include, for example, gelatin, gelatin derivatives such as phthalated gelatin and benzenesulfonyl gelatin, water-soluble natural macromolecular materials such as agar, casein, and alkyne carboxylic acid, synthetic resins such as polyvinyl alcohol and polyvinyl pyrrolidone, and cellulose derivatives such as carboxymethyl cellulose. These hydrophilic colloids may be used independently or in combination.
- 15 The silver halide emulsions applicable to the photographic materials of the invention contain any silver halide which is usually used in a silver halide photographic emulsion, such as silver chloride, silver bromide, silver iodide, silver chlorobromide, silver iodobromide, and a silver chloroiodobromide.
- 20 The silver halide emulsions applicable to the photographic materials of the invention may be prepared in various methods having been usually carried out. The preparation methods include, for example, the conversion method described in Japanese Patent Examined Publication No. 46-7772(1971), or the method described in U.S. Patent No. 2,592,250; and the so-called Lippmann emulsion preparation method, wherein the emulsion is comprised of a fine-grained silver halide having an average grain-size of not larger than 0.1 μ . The above-mentioned silver halide emulsions may be sensitized with a chemical sensitizer including, for example; a sulfur-sensitizer such as thiosulfate, allylthiocarbamide, thiourea, allylisothiocyanate or cystine; an active or inactive selenium sensitizer; a noble-metal sensitizer such as a gold compound, e.g., potassium chloroaurate, auric trichloride, potassium aurithiocyanate or 2-aurothiabenzothiazole methylchloride, a palladium compound, e.g., ammonium chloropalladate or sodium chloropalladite, a platinum compound, e.g., potassium chloroplatinate, a ruthenium compound, a rhodium compound, and an iridium compound; and the combination of the above-given sensitizers.
- 25 Besides the chemical sensitization, these emulsions may also be reduction-sensitized with a reducing agent, and they may further be stabilized with triazoles, imidazoles, azaindenes, benzthiazolium compounds, zinc compounds, cadmium compounds, mercaptans, or the mixtures thereof. Still further, the emulsions may contain a sensitizing compound such as thioethers, quaternary ammonium salts or polyalkylene oxides.
- 30 The photographic emulsions applicable to the photographic materials of the invention may be spectrally sensitized with a sensitizing dye, if required. Such sensitizing dyes applicable thereto include various dyes, for example, cyanine dyes, merocyanine dyes, complex cyanine dyes, oxonol dyes, hemioxonol dyes, styryl dyes, merostyryl dyes and streptocyanines. These sensitizing dyes may also be used independently or in combination.
- 35 In the photographic materials of the invention, the photographic emulsion layers and other hydrophilic colloidal layers thereof may contain glycerol, dihydroxyalkanes such as 1,5-pentanediol, esters such as ethylenebisglycol, bis-ethoxydiethyleneglycol succinate, and a water-dispersible fine-grained macromolecular compound prepared by an emulsification-polymerization, as wetting agents plasticizers, and physical surface property improving agents. Besides the above, they may also contain photographic additives including, for example, hardeners such as aldehyde compounds, N-methylol compounds, e.g., N,N'-dimethylol urea, active halogen compounds, e.g., mucohalogeno-acid, divinyl sulfones and 2,4-dichloro-6-hydroxy-5-triazine, dioxane derivatives, divinyl ketones, isocyanates and carbodiimides; surfactants such as saponin, polyalkylene glycol, polyalkylene glycol ether, alkylsulfonates, alkylbenzenesulfonate and alkylnaphthalenesulfonate; and, in addition, fluorescent brightening agents, antistatic agents, antistaining agents, UV absorbents, and stabilizers.
- 40 In the photographic materials of the invention, the photographic emulsion layers thereof may contain color couplers. Such color couplers may be of the 4- or 2-equivalent type, and they may also be a colored coupler for masking use or a coupler capable of releasing a development inhibitor. The yellow-forming couplers include, for example, an open-chained ketomethylene type compound such as those of the acylacetamide type; the magenta-forming couplers include, for example, a pyrazolone type compound; and the cyan-forming couplers include, for example, a phenol type or naphthol type compound, each has been advantageously used in general.

EXAMPLES

The invention will now be detailed with reference to the examples thereof. It is, however, to be
5 understood that the invention shall not be limited thereto.

Example 1

10 Gelatin in an amount of 3.5 g was dissolved into 35 ml of distilled water. Thereto, 5 ml of an aqueous solution containing 2.0×10^{-4} mols of an inventive dye or a comparative dye was added and, further, 1.25 ml of an aqueous 10% saponin solution and 0.75 ml of an aqueous 1% formalin solution was then added. After then, water was added thereto to make 50 ml in total. The resulting aqueous dye solution was coated over
15 an acetyl cellulose support and dried, so that Samples 1 through 35 were prepared. The samples were processed respectively with a simulant exhausted processing solution into which the following dye was accumulated.

20 Each of the samples was dipped in a sodium hydroxide solution having a pH of 10.4 containing the same dye compound as that of the sample having a mol-concentration of $10/C_A$ at $30^\circ C$ for 30 seconds with stirring. C_A represents a mol absorption coefficient of the dye, and so forth. The sample was washed for 15 seconds with water containing the same dye having a mol-concentration of $1/C_A$ in a tank, and dried.

25 The visible ray spectra of each sample obtained before and after dipping were measured and the elution ratio was obtained from the absorbance in the maximum absorption wavelength, and the result thereof is shown in Table-1.

$$\text{Elution ratio} = \frac{E_1 - E_2}{E_1} \times 100 \ (%)$$

30 wherein E_1 represents an absorbance obtained before a sample was dipped in an aqueous sodium hydroxide solution, and E_2 represents an absorbance obtained after dipping it.

35 On the other hand, each sample was dipped in the developer having the following composition at $30^\circ C$ for 30 seconds with stirring. The sample was washed with water containing the dye, that is the same as that of the sample, having a mol-concentration of $1/C_A$ in a tank for 15 seconds, and dried.

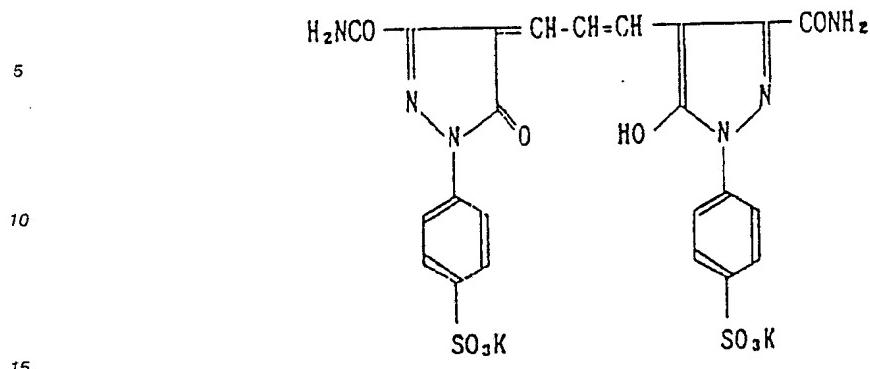
The visible ray spectra of each sample obtained before and after dipping it were measured to obtain the decoloration ratio from the absorbance in the maximum absorption wavelength. The result thereof is shown in Table-1.

$$\text{Decoloration ratio} = \frac{E_3 - E_4}{E_3} \times 100 \ (%)$$

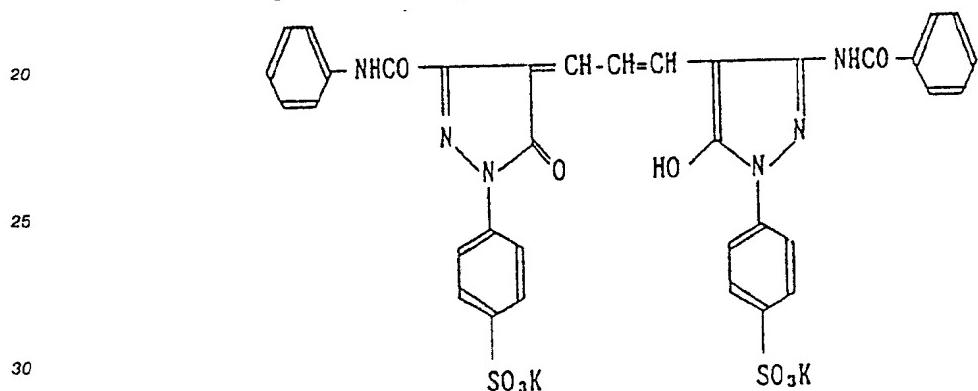
45 wherein E_3 represents an absorbance obtained before a sample was dipped in a developer, and E_4 represents an absorbance obtained after dipping it.

<Composition of Developer>	
Metol	3.0 g
Sodium sulfite, anhydrous	45.0 g
Sodium carbonate, monohydrate	80.0 g
Potassium bromide	2.0 g
Dye (Molecular weight) $\times(10/C_A)$ g	
Add water to make	1 liter

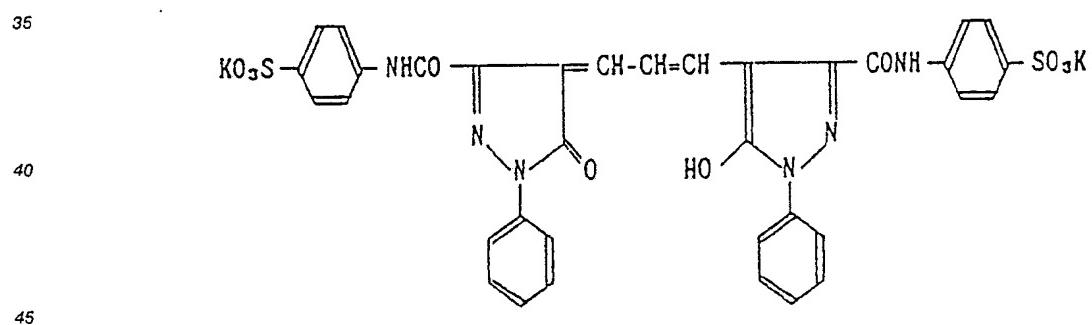
<Comparative dye A>



<Comparative dye B>



<Comparative dye C>



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<Comparative dye D>

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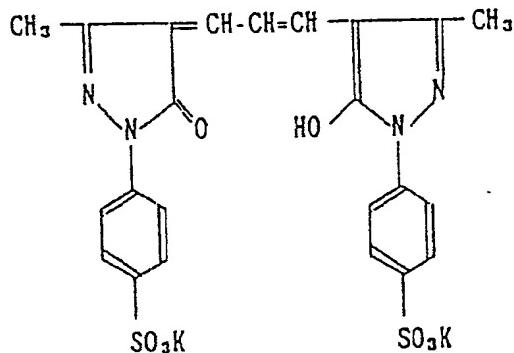


Table-1

	Sample No.	Dye	Elution ratio (%)	Decoloration ratio (%)	
5	1	Exemplified compound 1	95	97	Invention
	2		94	96	
	3		93	96	
	4		94	96	
	5		96	98	
	6		97	100	
	7		93	98	
	8		93	96	
	9		96	100	
	10		95	97	
10	11		94	97	
	12		96	98	
	13		96	98	
	14		96	100	
	15		94	98	
	16		95	99	
	17		96	99	
	18		95	97	
	19		96	98	
	20		93	97	
15	21		96	98	
	22		92	95	
	23		91	94	
	24		92	95	
	25		92	95	
	26		91	94	
	27		92	95	
	28		92	95	
	29		90	93	
	30		90	93	
20	31		90	93	
	32	Comparative dye A	86	90	
	33	B	85	90	
	34	C	84	89	
	35	D	86	88	

As is obvious from Table-1, the samples of the invention show very high values in both elution ratio and decoloration ratio, and the exemplified dyes of the invention can readily elute from gelatin layers and show excellent decoloring property as compared with the comparative dyes.

Example 2

50

A color light-sensitive material for color-printing use was prepared in the following manner. The resulting light-sensitive material sample was exposed imagewise to light and was then processed with the following color developer and bleach-fixer. With each of the dye images thereby formed, the characteristics were measured.

Preparation of Sample.

A sample was prepared in the following manner. The surface of a paper support was laminated with polyethylene containing anatase type titanium oxide serving as a white pigment. The resulting paper support was pre-treated by subbing gelatin and was then coated thereon with the following layer in order.

5

Layer 1 : Blue light-sensitive silver chlorobromide emulsion layer

A layer containing a silver chlorobromide emulsion having the silver chloride content of 5 mol%, and a dispersion prepared by dissolving the following yellow couplers Y-1 and 2,5-di-tert-octylhydroquinone in
10 dioctyl phthalate.

Layer 2 : First interlayer

15 A layer a dispersion prepared by dissolving 2,5-di-tert-octylhydroquinone in dioctyl phthalate.

Layer 3 : Green light-sensitive silver chlorobromide emulsion layer

20 A layer containing a silver chlorobromide emulsion having the silver chloride content of 15 mol%, a dispersion prepared by dissolving the following magenta coupler M-1 and 2,5-di-tert-octylhydroquinone in dioctyl phthalate, and an aqueous dye solution shown in the following Table-3.

25 Layer : 4 Second interlayer

A layer containing a dispersion prepared by dissolving the following UV absorbent UV-1 and 2,5-di-tert-octylhydroquinone, and an aqueous dye solution shown in Table-3.

30

Layer 5 : Red light-sensitive silver chlorobromide emulsion layer

A layer containing a silver chlorobromide emulsion having the silver chloride content of 25 mol%, and an emulsified dispersion prepared by dissolving the following cyan coupler C-1 and 2,5-di-tert-octylhydroquinone in dioctyl phthalate.
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Layer 6 : Protective layer

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A layer was containing gelatin and a hardener.

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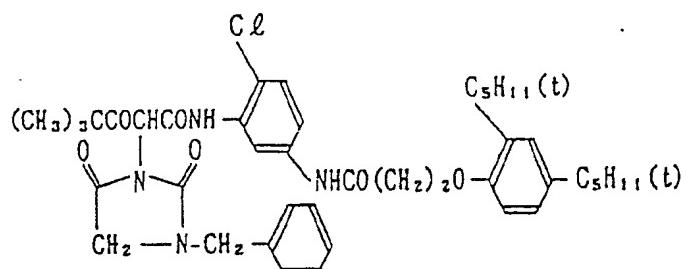
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Y-1

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M-1

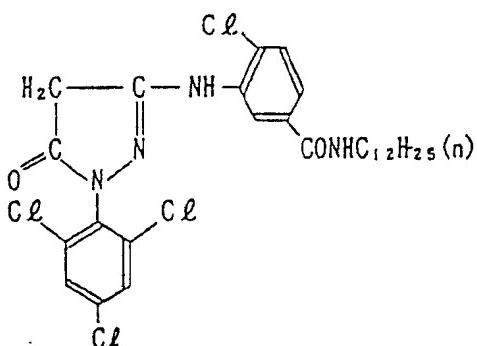
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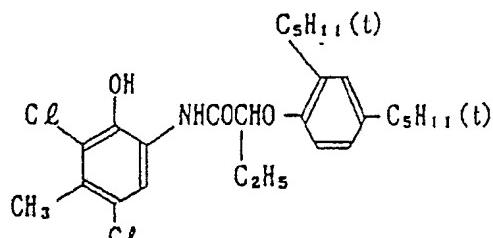
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C-1

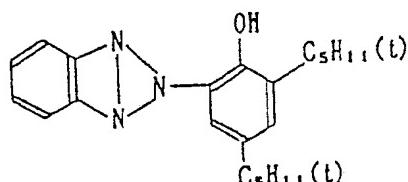
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UV-1

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The following Table-2 shows the quantity of each component of the above-mentioned sample, in terms of milligrams per 100 cm².

Table 2

Layer No.	Silver halide emulsion	UV absorbent or Coupler	2,5-di-t-octyl hydroquinone	Gelatin
1	Blue-sensitive silver chlorobromide emulsion, 3 mg in terms of silver	Y-1 8 mg	0.5 mg	20 mg
2	Interlayer	-	1.0 mg	10 mg
3	Green-sensitive silver chlorobromide emulsion, 4 mg in terms of silver	M-1 5 mg	0.5 mg	15 mg
4	Interlayer	UV-1 6 mg	1.0 mg	10 mg
5	Red-sensitive silver chlorobromide emulsion, 3 mg in terms of silver	C-1 4 mg	0.5 mg	15 mg
6	Protective layer	-	-	10 mg

According to the layer arrangement described above, in the green-sensitive silver chlorobromide emulsion layer and Layer 4 that was the interlayer, the dyes of such layers were changed, so that the samples shown in Table-3 were prepared. On the other hand, in the red-sensitive silver chlorobromide 5 emulsion layer and Layer 4 that was the interlayer, the dyes of such layers were changed, so that the samples shown in Table-4 were prepared. With the resulting samples, the following items were evaluated.

<1> Fog

10 Unexposed samples were processed in the following processing steps. The magenta and cyan density of the resulting samples were measured with a densitometer Model D-122 manufactured by Gretag.

15 <2> Residual color stain

For investigating the degrees of colored stains caused by the residual colors of the dyes after the samples were processed, the same solution as the color developer used in the processing steps mentioned 20 in the Example 1, except that N-ethyl-N- β -methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate was not used in the developer, and the same tests as mentioned in Example 1 were tried. The results thereof are shown in Tables-3 and 4. The residual color stain is mentioned simply as 'stain' in the tables.

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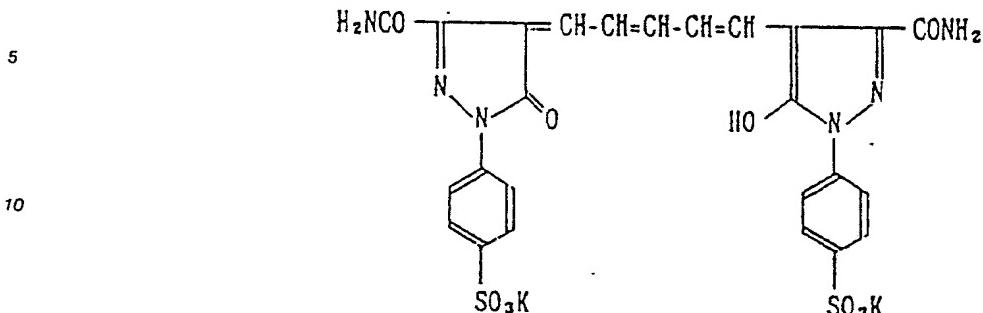
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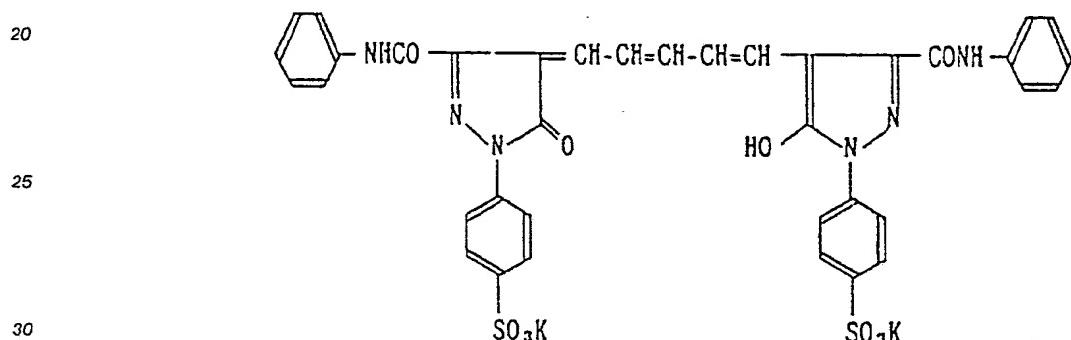
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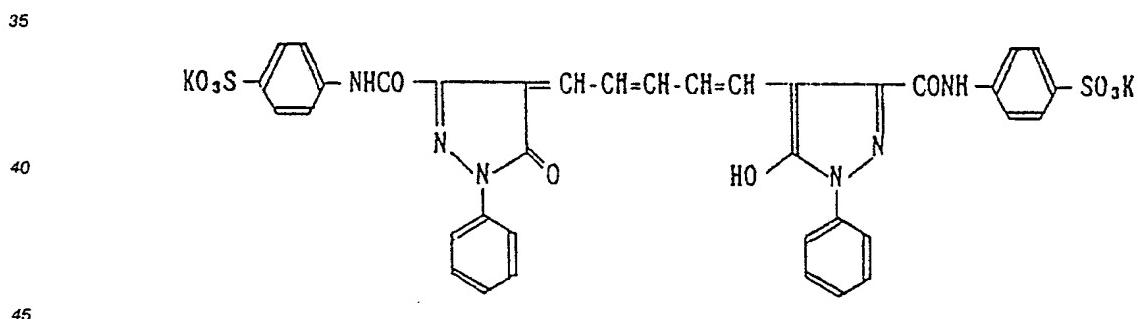
Comparative dye E



Comparative dye F



Comparative dye G



Processing steps -carried out at 38 ° C-	
Color developing	2 min. 30 sec.
Bleach-fixing	1 min.
Washing	1 min.
Drying	60 to 80 ° C, 2 min.

50

Color developing	2 min. 30 sec.
Bleach-fixing	1 min.
Washing	1 min.
Drying	60 to 80 ° C, 2 min.

55

The composition of each processing solution was as follows.

<Color developer>		
5	Pure water	800 ml
	Benzyl alcohol	15 ml
	Triethanolamine	10 g
	Hydroxylamine sulfate	2.0 g
	Potassium bromide	1.5 g
	Sodium chloride	1.0 g
	Potassium sulfite	2.0 g
10	N-ethyl-N- β -methanesulfonamido-ethyl-3-methyl-4-aminoaniline sulfate	4.5 g
	1-hydroxyethylidene-1,1-diphosphonate, in an aqueous 60% solution	1.5 ml
	Potassium carbonate	32 g
15	Whitex BB, a fluorescent brightening agent manufactured by Sumitomo Chemical Co., in an aqueous 50% solution	2 ml
	Add pure water to make	1 liter
	Adjust pH with a 20% potassium hydroxide or 10% sulfuric acid solution to	pH 10.1
20		

<Bleach-fixer>		
25	Pure water	600 ml
	Ferric ammonium ethylenediaminetetraacetate	65 g
	Disodium ethylenediaminetetraacetate	5 g
	Ammonium thiosulfate	85 g
	Sodium hydrogensulfite	10 g
	Sodium metabisulfite	2 g
30	Add pure water to make	1 liter
	Adjust pH with dilute sulfuric acid to	pH = 7.0

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Table 3

5	Sample No.	Dye in green-sensitive AgClBr emulsion layer	Dye in inter-layer <Layer-4>	Reflection density in unexposed area	
				(1) Fog	(2) Stain
10	36	----	----	0.002	0
15	37	Exemplified compound 3 0.08	----	0.004	0.002
20	38	-ditto- 3 0.16	----	0.006	0.005
25	39	-----	Exemplified compound 7 0.08	0.003	0.002
30	40	Exemplified compound 7 0.08	-ditto- 7 0.16	0.007	0.005
35	41	-ditto- 7 0.08	----	0.003	0.002
40	42	-----	Exemplified compound 12 0.08	0.004	0.003
45	43	Exemplified compound 12 0.08	----	0.004	0.002
50	44	-----	Exemplified compound 14 0.08	0.004	0.003
55	45	Exemplified compound 14 0.08	----	0.004	0.003
60	46	-ditto- 16 0.08	----	0.003	0.002
65	47	-ditto- 16 0.16	----	0.005	0.003
70	48	-----	Exemplified compound 18 0.08	0.006	0.004
75	49	Exemplified compound 24 0.08	----	0.003	0.002
80	50	-----	Exemplified compound 24 0.08	0.003	0.002

- to be continued -

Table 3 (Continued)

5	Sample No.	Dye in green-sensitive AgClBr emulsion layer	Dye in inter-layer (Layer-4)	Reflection density in unexposed area		
				(1) Fog	(2) Stain	
10	51	Exemplified compound 29 0.08	----	0.004	0.002	Sample in the Inv.
15	52	-ditto- 33 0.04	----	0.005	0.003	-ditto-
20	53	-ditto- 52 0.08	----	0.007	0.005	-ditto-
25	54	----	Exemplified compound 79 0.08	0.007	0.005	-ditto-
30	55	Comparative dye A 0.08	----	0.009	0.008	Comp. Sample
35	56	-ditto- B 0.16	----	0.013	0.011	-ditto-
40	57	----	Comparative dye B 0.08	0.009	0.008	-ditto-
45	58	Comparative dye C 0.08	----	0.012	0.010	-ditto-
50	59	----	Comparative dye C 0.08	0.012	0.010	-ditto-

Table 4

5	Sample No.	Dye in red-sensitive AgClBr emulsion layer	Dye in inter-layer <Layer-4>	Reflection density in unexposed area		Comp. Sample
				(1) Fog	(2) Stain	
10	60	----	----	0.003	0	Comp. Sample
15	61	Exemplified compound 1 0.08	----	0.004	0.002	Sample in the Inv.
20	62	-ditto- 1 0.16	----	0.005	0.003	-ditto-
25	63	----	Exemplified compound 1 0.08	0.004	0.003	-ditto-
30	64	Exemplified compound 1 0.08	-ditto- 1 0.16	0.006	0.004	-ditto-
35	65	-ditto- 2 0.08	----	0.005	0.003	-ditto-
40	66	----	Exemplified compound 2 0.08	0.005	0.003	-ditto-
45	67	Exemplified compound 5 0.08	----	0.004	0.002	-ditto-
50	68	----	Exemplified compound 5 0.08	0.004	0.002	-ditto-
55	69	Exemplified compound 6 0.08	----	0.004	0.002	-ditto-
60	70	-ditto- 10 0.08	----	0.004	0.003	-ditto-
65	71	-ditto- 13 0.16	----	0.007	0.005	-ditto-
70	72	----	Exemplified compound 13 0.08	0.005	0.003	-ditto-
75	73	Exemplified compound 16 0.08	----	0.005	0.003	-ditto-
80	74	----	Exemplified compound 16 0.08	0.005	0.002	-ditto-

- to be continued -

Table 4 (Continued)

5	Sample No.	Dye in red-sensitive AgClBr emulsion layer	Dye in inter-layer <Layer-4>	Reflection density in unexposed area	
				(1) Fog	(2) Stain
10	75	Exemplified compound 17	0.08	----	0.006 0.004
15	76	-ditto-	20 0.04	Exemplified compound 20 0.08	0.004 0.003
20	77	-ditto-	45 0.08	----	0.007 0.005
25	78	----		Exemplified compound 81 0.08	0.007 0.005
30	79	Comparative dye E	0.08	----	0.010 0.009
35	80	-ditto-	F 0.16	----	0.014 0.011
40	81	----		Comparative dye F 0.08	0.012 0.010
45	82	Comparative dye G	0.08	----	0.013 0.011
50	83	----		Comparative dye G 0.08	0.013 0.011

35 In Tables 3 and 4, the numerals of the dyes indicate an amount of mg coated per 100 cm².
 The desired whiteness of color light-sensitive materials for printing use is required to be not more than 0.005 in terms of fogginess. It is obvious from Tables 3 and 4 that the samples of the invention satisfy the requirement. In the samples of the invention, there was scarcely found such a colored stain caused by the residual colors of dyes as often found in the samples containing the comparative dyes. In other words, it was found that the dyes of the invention exert very few bad influences on emulsions.

Example 3

45 Comparative multilayered color light-sensitive material sample No. 84 was prepared in such a manner that each of the layers having the following compositions was coated over a subbed triacetyl cellulose film support, in order from the support side. The amount of each component coated are expressed in terms of g/m².

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Layer 1: An antihalation layer	
UV absorbent, U-1	0.3
UV absorbent, U-2	0.4
High boiling solvent, O-1	1.0
Black colloidal silver	0.24
Gelatin	2.0

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Layer 2: An interlayer	
2,5-di-t-octylhydroquinone	0.1
High boiling solvent, O-1	0.2
Gelatin	1.0

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Layer 3: A low-speed red-sensitive silver halide emulsion layer

AgBrI emulsion having an AgI content of 4.0 mol% and an average particle-size of 0.25 μ , spectrally sensitized with red-sensitizing dyes S-1 and S-2	0.5
coupler, C-1	0.1 mol
High boiling solvent, O-2	0.6
Gelatin	1.3

30

Layer 4: A high-speed red-sensitive silver halide emulsion layer

AgBrI emulsion having an AgI content of 2.0 mol% and an average particle-size of 0.6 μ , spectrally sensitized with red-sensitizing dyes S-1 and S-2	0.8
coupler, C-1	0.2 mol
High boiling solvent, O-2	1.2
Gelatin	1.8

40

Layer 5: An interlayer

2,5-di-t-octylhydroquinone	0.1
High boiling solvent, O-1	0.2
Gelatin	0.9

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Layer 6: A low-speed green-sensitive silver halide emulsion layer

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	AgBrI emulsion having an AgI content of 4.0 mol% and an average particle-size of 0.25 μ , spectrally sensitized with green-sensitizing dyes S-3 and S-4	0.6
5	coupler, C-2	0.04 mol
	coupler, C-3	0.01 mol
10	High boiling solvent, O-3	0.5
	Gelatin	1.4

Layer 7: A high-speed green-sensitive silver halide emulsion layer		
	AgBrI emulsion having an AgI content of 2.0 mol% and an average particle-size of 0.6 μ , spectrally sensitized with green-sensitizing dyes S-3 and S-4	0.9
20	coupler, C-2	0.10 mol
	coupler, C-3	0.02 mol
	High boiling solvent, O-3	1.0
25	Gelatin	1.5

30 Layer 8: An interlayer

The same as Layer 5.

Layer 9: A yellow filter layer		
35	Yellow colloidal silver	0.1
	Gelatin	0.9
	2,5-di-t-octylhydroquinone	0.1
	High boiling solvent, O-1	0.2

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45 Layer 10: A low-speed blue-sensitive silver halide emulsion layer

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5	AgBrI emulsion having an AgI content of 4 mol% and an average particle-size of 0.35 μ , spectrally sensitized with blue-sensitizing dye S-5	0.6
	coupler, C-4	0.3 mol
10	High boiling solvent, O-3	0.6
	Gelatin	1.3

Layer 11: A high-speed blue-sensitive silver halide emulsion layer		
15	AgBrI emulsion having an AgI content of 2 mol% and an average particle-size of 0.9 μ , spectrally sensitized with blue-sensitizing dye S-5	0.9
20	coupler, C-4	0.5 mol
	High boiling solvent, O-3	1.4
	Gelatin	2.1

Layer 12: The first protective layer		
25	UV absorbent, U-1	0.3
	UV absorbent, U-2	0.3
30	High boiling solvent, O-3	0.6
	Gelatin	1.2
	2,5-di-t-octylhydroquinone	0.1

Layer 13: The second protective layer		
40	Non-light-sensitive fine-grained silver iodobromide emulsion having an average grain-size \bar{y} of 0.08 μ m and a silver iodide content of 1 mol% Polymethyl methacrylate particle having a particle-size of 1.5 μ m Gelatin	0.3 <In terms of silver> 0.7

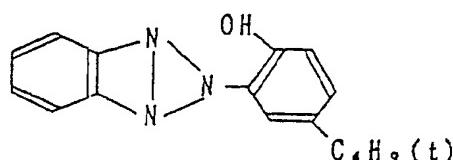
45 Besides the above-given compositions, each layer was added with gelatin-hardener 1 and a surfactant. Further, tricresyl phosphate was also used as the solvent of the couplers.

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UV absorbent U-1

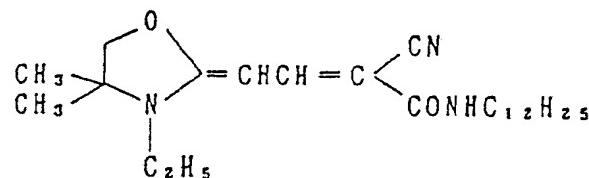
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UV absorbent U-2

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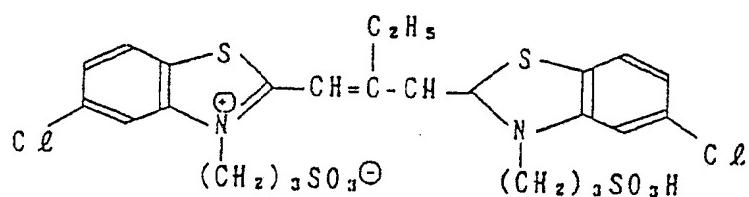


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Sensitizing dye S-1

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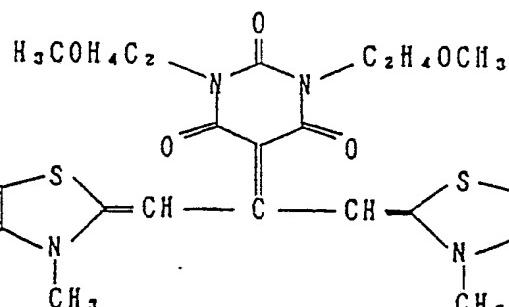
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Sensitizing dye S-2

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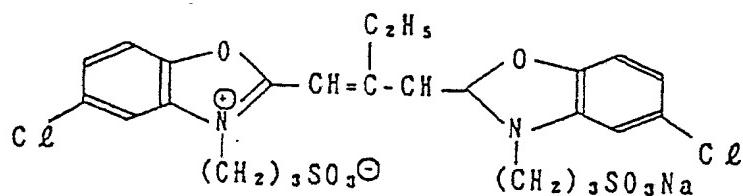
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Sensitizing dye S-3

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Sensitizing dye S-4

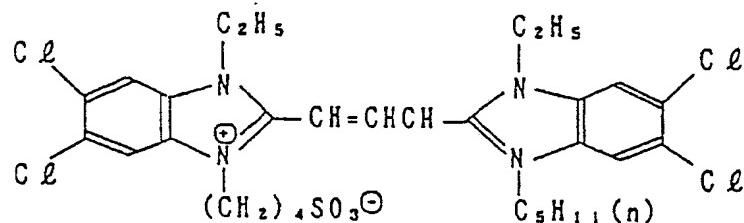
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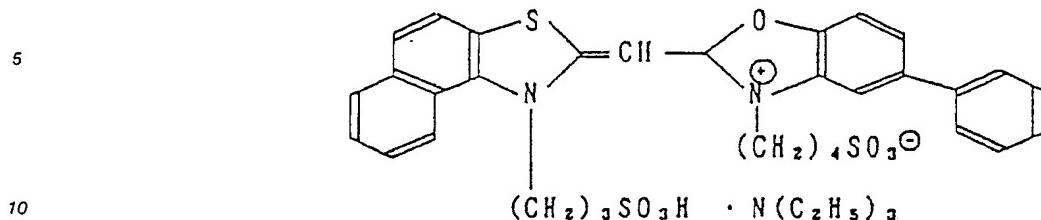
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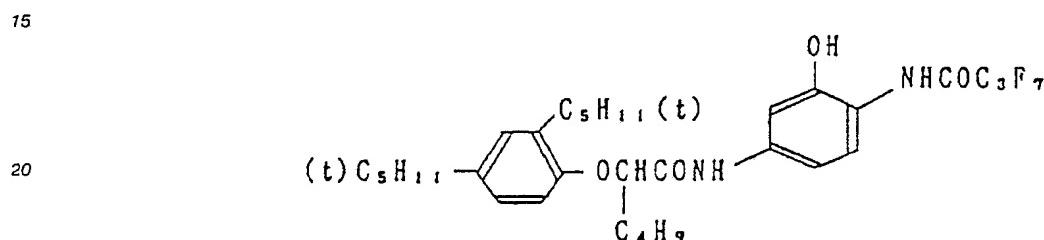
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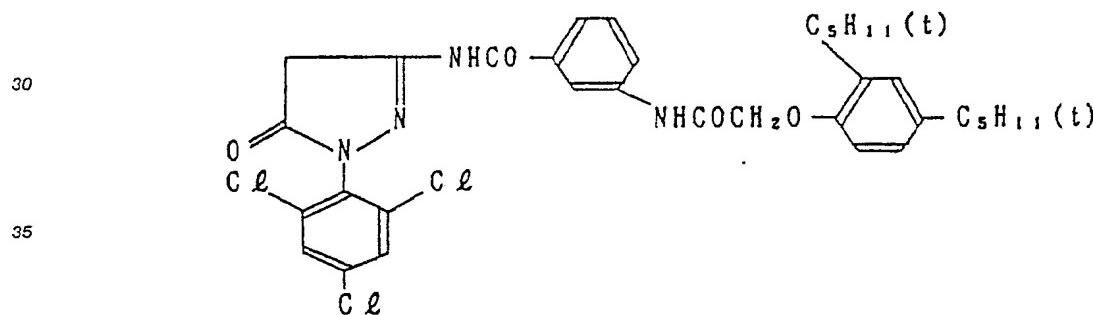
Sensitizing dye S-5



Coupler C-1



Coupler C-2



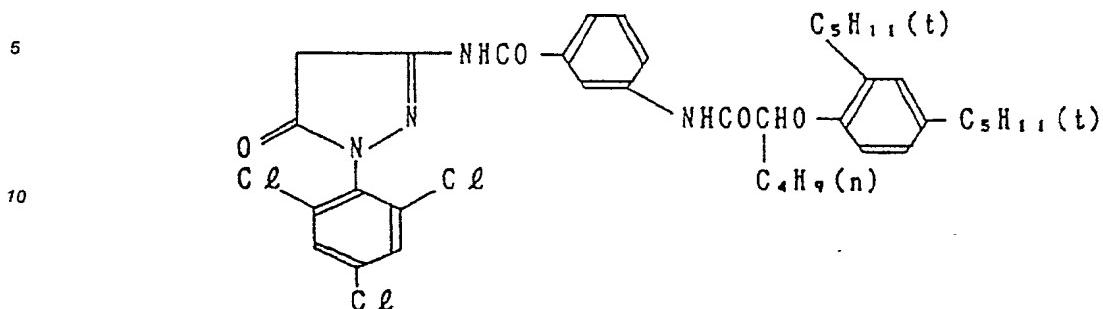
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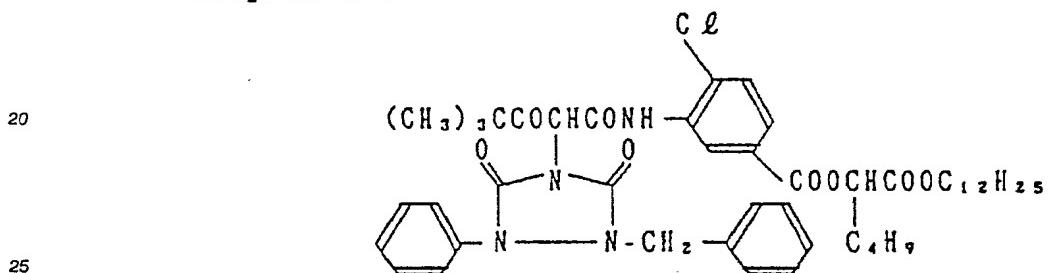
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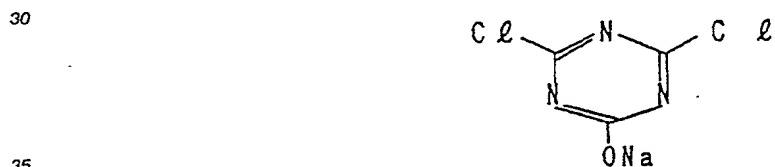
Coupler C-3



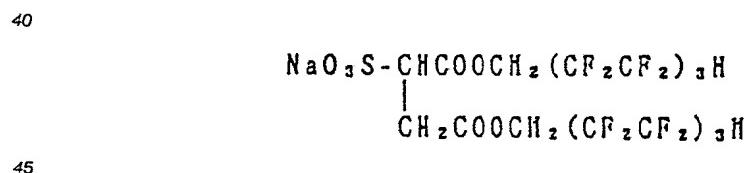
Coupler C-4



Gelatin hardener 1



Surfactant 1

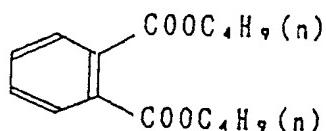


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O-1

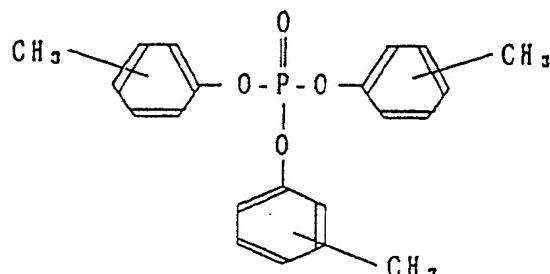
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O-2

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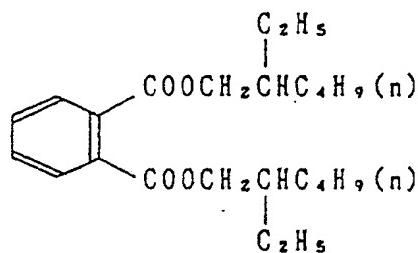


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O-3

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The samples shown in Table-5 were prepared by adding the compounds of the invention each in an amount of 0.01 g/m² into Layer 13, i.e., the second protective layer, of Sample No. 84, respectively. The resulting samples were evaluated as follows.

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< Fog >

After the unexposed samples were preserved at 55 °C for 7 days, they were processed in the following processing steps. The resulting increases, Δ Dmax, of the maximum blue-densities of the samples caused by the preservation were shown by the values relative to that of Sample No. 84 which is regarded as a value of 100.

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<Processing steps>			
	Step	Time	Temperature
5	First developing	6 min.	38 °C
	Washing	2 min.	38 °C
	Reversing	2 min.	38 °C
10	Color developing	6 min.	38 °C
	Moderating	2 min.	38 °C
	Bleaching	6 min.	38 °C
	Fixing	4 min.	38 °C
	Washing	4 min.	38 °C
	Stabilizing	1 min.	at ordinary temperature
15	Drying	-	-

The compositions of the processing solutions each used in the above-mentioned processing steps were as follows.

<First developer>			
20	Sodium tetrapolyphosphate	2 g	
	Sodium sulfite	20 g	
25	Hydroquinone monosulfonate	30 g	
	Sodium carbonate, monohydrate	30 g	
	1-phenyl-4-methyl-4-hydroxymethyl-3-pyrazolidone	2 g	
	Potassium bromide	2.5 g	
	potassium thiocyanate	1.2 g	
30	Potassium iodide, in an aqueous 0.1% solution	2 ml	
	Add water to make	1000 ml	

<Reversing solution>			
35	Hexasodium nitrilotrimethylenephosphonate	3 g	
	Stannous chloride, dihydrate	1 g	
	p-aminophenol	0.1 g	
40	Sodium hydroxide	8 g	
	Glacial acetic acid	15 ml	
	Add water to make	1000 ml	

<Color developer>			
50	Sodium tetrapolyphosphate	3 g	
	Sodium sulfite	7 g	
	Trisodium phosphate, dihydrate	36 g	
	Potassium bromide	1 g	
	Potassium iodide, in an aqueous 0.1 % solution	90 ml	
	Sodium hydroxide	3 g	
55	Citrazinic acid	1.5 g	
	N-ethyl-N-β-methanesulfonamidoethyl-3-methyl-4-aminoaniline sulfate	11 g	
	2,2-ethylenedithiodiethanol	1 g	
	Add water to make	1000 ml	

<Moderating solution>			
5	Sodium sulfite	12 g	
	Sodium ethylenediaminetetraacetate, dihydrate	8 g	
	Thioglycerol	0.4 ml	
	Glacial acetic acid	3 ml	
	Add water to make	1000 ml	

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<Bleaching solution>			
15	Sodium ethylenediaminetetraacetate, dihydrate	2 g	
	Ferric ammonium ethylenediamine tetraacetate, dihydrate	120 g	
	Ammonium bromide	100 g	
	Add water to make	1000 ml	

<Fixing solution>			
25	Ammonium thiosulfate	80 g	
	Sodium sulfite	5 g	
	Sodium bisulfite	5 g	
	Add water to make	1000 ml	

<Stabilizer>			
35	Formalin, at 37 % by weight	5 ml	
	Konidux, manufactured by Konica Corp.	5 ml	
	Add water to make	1000 ml	

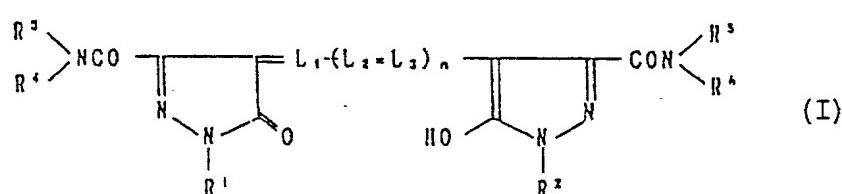
Table-5

Sample No.	Dye	Dmax	
84	-	100	Comparative
85	Exemplified Compound 1	100	Invention
86	Exemplified Compound 2	99	Invention
87	Exemplified Compound 3	100	Invention
88	Exemplified Compound 7	100	Invention
89	Exemplified Compound 10	99	Invention
90	Exemplified Compound 14	100	Invention
91	Exemplified Compound 17	98	Invention
92	Exemplified Compound 18	98	Invention
93	Exemplified Compound 21	100	Invention
94	Exemplified Compound 22	99	Invention
95	Exemplified Compound 24	100	Invention
96	Exemplified Compound 26	100	Invention
97	Exemplified Compound 41	98	Invention
98	Exemplified Compound 53	98	Invention
99	Exemplified Compound 55	98	Invention
100	Exemplified Compound 61	98	Invention
101	Comparative dye A	87	Comparative
102	Comparative dye B	85	Comparative
103	Comparative dye C	83	Comparative
104	Comparative dye D	86	Comparative
105	Comparative dye E	88	Comparative
106	Comparative dye F	87	Comparative

As is obvious from the results shown in Table-5, it is found that the dyes of the invention did scarcely affect emulsion performance, that is, the dyes of the invention are inactive to emulsions.

Claims

1. A silver halide photographic light-sensitive material containing a water-soluble oxonol dye represented by the following Formula 1:



wherein R¹ and R² are each a hydrogen atom, an alkyl group, an aryl group or an alkenyl group; R³, R⁴, R⁵ and R⁶ are each a hydrogen atom, an alkyl group, an aryl group, an alkenyl group or a heterocyclic group provided that at least one of said R³, R⁴, R⁵ and R⁶ is a heterocyclic group and R³ and R⁴, and R⁵ and R⁶ are respectively allowed to bond to form a heterocyclic ring; and the groups represented by said R¹ through R⁶ are allowed to be substituted or unsubstituted provided that at least one of said groups is a water-solubilizing group or a group having a water-solubilizing group; L₁, L₂ and L₃ are each a substituted or unsubstituted methine group; and n is an integer of zero, 1 or 2.

2. The material of claim 1, wherein said heterocyclic group represented by said R³, R⁴, R⁵ or R⁶ is a pyridyl group, an oxazolyl group, a thiazolyl group, an imidazolyl group, a furyl group, a pyrrolyl group, a

thienyl group, a pyrazinyl group, a pyrimidinyl group, a pyridazinyl group, a purinyl group, an isoazolinyl group, a selenazolinyl group, a sulfolanyl group, a piperidinyl group, a pyrazolyl group or a tetrazolyl group, provided that these groups allowed to have a substituent.

3. The material of claim 1, wherein said R³ and R⁵ are each a hydrogen atom or an alkyl group; and R⁴ and R⁶ are each a heterocyclic group.

4. The material of claim 3, wherein said R³ and R⁵ are each a hydrogen atom; and R⁴ and R⁶ are each a heterocyclic group.

5. The material of claim 4, wherein said heterocyclic groups represented by said R⁴ and R⁶ are the same with each other and nitrogen atoms of the amido groups at the third position of the pyrazolone rings of Formula 1 are each directly bonded with carbon atom of each of said heterocyclic groups.

6. The material of claim 1, wherein said water-solubilizing group is a sulfo group, a sulfinyl group, a carboxy group, a phosphono group a phosphoryl group a hydroxy group or a sulfic ester group.

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